

Note re: WordPerfect 6.1 file of NMOG TPs:

The following portions of this document are not in the WordPerfect file and need to be hand inserted:

Struck out facesheets for Parts B, C, D, E, F and G.

California Environmental Protection Agency
AIR RESOURCES BOARD

**CALIFORNIA NON-METHANE ORGANIC GAS
TEST PROCEDURES**

Adopted: July 12, 1991
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Mobile Source Division
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NOTE: Mention of any trade name or commercial product does not constitute endorsement or recommendation of this product by the Air Resources Board.

The regulatory amendments adopted in this rulemaking are shown in underline to indicate additions and ~~strikeout~~ to indicate deletions from the version of the test procedures adopted on September 22, 1993.

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Part A

GENERAL APPLICABILITY AND REQUIREMENTS

1. These test procedures shall apply to all 1993 and subsequent model-year transitional low-emission vehicles (TLEV), low-emission vehicles (LEV), and ultra low-emission vehicles (ULEV) certifying to non-methane organic gas (NMOG) emission standards.
2. This document sets forth the analysis and calculation procedures that shall be performed to determine NMOG mass emissions. The document consists of the following parts:
 - A. General Applicability and Requirements
 - B. Determination of Non-Methane Hydrocarbon Mass Emissions by Flame Ionization Detection
 - C. Determination of Alcohols in Automotive Source Samples by Gas Chromatography (Method No. 1001)
 - D. Determination of C₂ to C₅ Hydrocarbons in Automotive Source Samples by Gas Chromatography (Method No. 1002)
 - E. Determination of C₆ to C₁₂ Hydrocarbons in Automotive Source Samples by Gas Chromatography (Method No. 1003)
 - F. Determination of Aldehyde and Ketone Compounds in Automotive Source Samples by High Performance Liquid Chromatography (Method No. 1004).
 - G. Determination of NMOG Mass Emissions

Appendix 1 List of Light-End and Mid-Range Hydrocarbons

Appendix 2 Definitions and Commonly Used Abbreviations

Appendix 3 References

Alternative procedures may be used if shown to yield equivalent results and if approved in advance by the Executive Officer of the Air Resources Board.

3. The analyses specified in the table below shall be performed to determine mass emission rates of NMOG in grams per mile (g/mi) or milligrams per mile (mg/mi) for vehicles operated on the listed fuel:

Fuel	NMHC by FID	NMHC by GC	Alcohols	Carbonyls
Alcohol	X		X	X
CNG		X		X
Diesel	X			X
Gasoline	X			X
LPG	X			X

where "LPG" means "liquified petroleum gas", "CNG" means "compressed natural gas", "NMHC" means "non-methane hydrocarbon", "FID" means "flame ionization detector", and "GC" means "gas chromatograph." The specified analyses shall be performed in accordance with the following parts of this document:

NMHC by FID	--	Part B.	Determination of Non-Methane Hydrocarbon Mass Emissions by Flame Ionization Detection
NMHC by GC	--	Part D.	Determination of C ₂ to C ₅ Hydrocarbons in Automotive Source Samples by Gas Chromatography (Method No. 1002); and
		Part E.	Determination of C ₆ to C ₁₂ Hydrocarbons in Automotive Source Samples by Gas Chromatography (Method No. 1003)
CARBONYLS	--	Part F.	Determination of Aldehyde and Ketone Compounds in Automotive Source Samples by High Performance Liquid Chromatography (Method No. 1004)
ALCOHOLS	--	Part C.	Determination of Alcohols in Automotive Source Samples by Gas Chromatography (Method No. 1001)

- 4 For those manufacturers which choose to develop reactivity adjustment factors unique to a specific engine family, exhaust NMOG emissions shall be fully speciated. NMHC emissions shall be analyzed in accordance with parts D and E (Method Nos. 1002 and 1003). In addition, aldehydes and ketones, alcohols, and ethers shall be analyzed according to parts F, C, and E (Method Nos. 1004, 1001, and 1003). Analysis for alcohols shall be required only for vehicles which are operated on fuels containing alcohols.
5. For natural gas-fueled vehicles, the methane concentration in the exhaust sample shall be measured with a methane analyzer. A GC combined with a FID is used for direct measurement of methane concentrations. SAE Recommended Practice J1151 is a reference on generally accepted GC principles and analytical techniques for this application. A density of 18.89 g/ft³ shall be used to determine the methane mass

emissions. The methane mass emissions shall be multiplied by the appropriate methane reactivity adjustment factor and then added to the reactivity-adjusted NMOG emissions as specified in "California Exhaust Emission Standards and Test Procedures for 1988 and Subsequent Model Passenger Cars, Light-Duty Trucks, and Medium-Duty Vehicles."

6. The mass of NMOG emissions shall be calculated in accordance with part G, "Determination of NMOG Mass Emissions". The mass of NMOG emissions in g/mile or mg/mile shall be calculated by summing the mass of NMHC determined by the FID, the mass of aldehydes and ketones, and the mass of alcohols.

PART B

DETERMINATION OF
NON-METHANE HYDROCARBON MASS EMISSIONS
BY FLAME IONIZATION DETECTION

1. INTRODUCTION

1.1 This procedure describes a method for determining ~~non-methane hydrocarbon~~ (NMHC) exhaust mass emissions from motor vehicles. Other applicable forms of instrumentation and analytical techniques which prove to yield equivalent results to those specified in this procedure may be used subject to the approval of the Executive Officer of the Air Resources Board.

1.2 All definitions and abbreviations are contained in Appendix 2 of these test procedures.

2. TOTAL HYDROCARBON MEASUREMENT

2.1 A ~~flame ionization detector~~ (FID) is used to measure total hydrocarbon concentration in vehicle exhaust in accordance with the Code of Federal Regulations.[Ref 1] SAE Recommended Practices J254[Ref. 2] and J1094a[Ref. 3] are references on generally accepted gas analysis and constant volume sampling techniques. For Beckman 400 FIDs only, implementation of the recommendations outlined in SAE paper 770141; "~~Optimization of Flame Ionization Detector for Determination of Hydrocarbons in Diluted Automobile Exhaust,~~" author, Glenn D. Reschke[Ref. 4] shall be required. Other FID analyzer models shall be checked and adjusted, if necessary, to minimize any non-uniformity of relative response to different hydrocarbons.

3. METHANE MEASUREMENT

3.1 A ~~gas chromatograph~~ (GC) combined with a FID constitute a methane analyzer and shall be used for direct measurement of methane concentrations. The SAE Recommended Practice J1151[Ref. 5] is a reference on generally accepted GC principles and analytical techniques for this specific application.

4. TOTAL HC FID RESPONSE TO METHANE

4.1 The FID is calibrated to propane and therefore tends to over respond to the methane portion of the vehicle exhaust sample during hydrocarbon analysis. In order to calculate the NMHC concentration, a methane response factor must be applied to the methane concentration (as measured by the methane analyzer) before it can be deducted from the total hydrocarbon concentration. To determine the total hydrocarbon FID response to methane, known methane in air concentrations traceable to ~~National Institute of Standards and Technology~~ (NIST) shall be analyzed by the FID. Several methane concentrations

shall be analyzed by the FID in the range of the exhaust sample concentration. The total hydrocarbon FID response to methane is calculated as follows:

$$r_{CH_4} = FID_{ppm}/SAM_{ppm}$$

where:

$$\begin{aligned} r_{CH_4} &= \text{FID methane response factor.} \\ FID_{ppm} &= \text{FID reading in ppmC.} \\ SAM_{ppm} &= \text{the known methane concentration in ppmC.} \end{aligned}$$

The FID response to methane shall be checked at each calibration interval.

5. NMHC MASS EMISSION PER TEST PHASE

5.1 The following calculations shall be used to determine the NMHC mass emissions for each phase of the Federal Test Procedure. [Ref. 1].

5.2 Non-Alcohol Fueled Vehicles

5.2.1 $NMHC_e = FID\ THC_e - (r_{CH_4} * CH_{4e})$

NOTE: If $NMHC_e$ is calculated to be less than zero, then $NMHC_e = 0$.

5.2.2 $NMHC_d = FID\ THC_d - (r_{CH_4} * CH_{4d})$

NOTE: If $NMHC_d$ is calculated to be less than zero, then $NMHC_d = 0$.

5.2.3 $CO_e = (1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a) * CO_{em}$

NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e .

a) For gasoline, $CH_{1.85}$, where $HCR = 1.85$:

$$CO_e = (1 - 0.01925 * CO_{2e} - 0.000323 * R_a) * CO_{em}$$

b) For Phase 2 gasoline, $CH_{1.94}$, where $HCR = 1.94$:

$$CO_e = (1 - 0.01970 * CO_{2e} - 0.000323 * R_a) * CO_{em}$$

b_c) For LPG, $CH_{2.66\ 2.64}$, where $HCR = 2.66\ 2.64$:

$$CO_e = (1 - 0.02330\ 0.02320 * CO_{2e} - 0.000323 * R_a) * CO_{em}$$

d) For CNG, $CH_{3.78}$, where $HCR = 3.78$:

$$CO_e = (1 - 0.02890 * CO_{2e} - 0.000323 * R_a) * CO_{em}$$

$$5.2.4\ DF = \frac{100 * \frac{x}{x + y/2 + 3.76 * (x + y/4 - z/2)}}{CO_{2e} + (NMHC_e + CH_{4e} + CO_e) * 10^{-4}}$$

(where fuel composition is $C_xH_yO_z$ as measured for the fuel used.)

- a) For gasoline, $\text{CH}_{1.85}$, where $x = 1$, $y = 1.85$, and $z = 0$:
 $\text{DF} = 13.47 / [\text{CO}_{2e} + (\text{NMHC}_e + \text{CH}_{4e} + \text{CO}_e) * 10^{-4}]$
- b) For Phase 2 gasoline, $\text{CH}_{1.94}$, $x = 1$, $y = 1.94$ and $z = 0.017$:
 $\text{DF} = 13.29 / [\text{CO}_{2e} + (\text{NMHC}_e + \text{CH}_{4e} + \text{CO}_e) * 10^{-4}]$
- c) For LPG, $\text{CH}_{2.66}$, where $x = 1$, $y = 2.66$, and $z = 0$:
 $\text{DF} = 11.64 / [\text{CO}_{2e} + (\text{NMHC}_e + \text{CH}_{4e} + \text{CO}_e) * 10^{-4}]$
- d) For CNG, $\text{CH}_{3.78}$, where $x = 1$, $y = 3.78$, and $z = 0.016$:
 $\text{DF} = 9.83 / [\text{CO}_{2e} + (\text{NMHC}_e + \text{CH}_{4e} + \text{CO}_e) * 10^{-4}]$

5.3 Vehicles Operating on Fuels Containing Methanol

5.3.1 $\text{NMHC}_e = \text{FID THC}_e - (r_{\text{CH}_4} * \text{CH}_{4e}) - (r_{\text{CH}_3\text{OH}} * \text{CH}_3\text{OH}_e)$
 NOTE: If NMHC_e is calculated to be less than zero, then $\text{NMHC}_e = 0$.

5.3.2 $\text{NMHC}_d = \text{FID THC}_d - (r_{\text{CH}_4} * \text{CH}_{4d}) - (r_{\text{CH}_3\text{OH}} * \text{CH}_3\text{OH}_d)$
 NOTE: If NMHC_d is calculated to be less than zero, then $\text{NMHC}_d = 0$.

5.3.3 $\text{CO}_e = (1 - (0.01 + 0.005 * \text{HCR}) * \text{CO}_{2e} - 0.000323 * R_a) * \text{CO}_{em}$
 NOTE: If a CO instrument which meets the criteria specified in CFR 40 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e .

a) For M100 (100% methanol), CH_3OH , where $\text{HCR} = 4$:
 $\text{CO}_e = (1 - 0.03000 * \text{CO}_{2e} - 0.000323 * R_a) * \text{CO}_{em}$

b) For M85 (85% methanol, 15% indolene), $\text{CH}_{3.41} \text{O}_{0.72}$, where $\text{HCR} = 3.41$:

$$\text{CO}_e = (1 - 0.02705 * \text{CO}_{2e} - 0.000323 * R_a) * \text{CO}_{em}$$

$$100 * \frac{x}{x + y/2 + 3.76 * (x + y/4 - z/2)}$$

5.3.4 $\text{DF} = \frac{100 * \frac{x}{x + y/2 + 3.76 * (x + y/4 - z/2)}}{\text{CO}_{2e} + (\text{NMHC}_e + \text{CH}_{4e} + \text{CO}_e + \text{CH}_3\text{OH}_e + \text{HCHO}_e) * 10^{-4}}$
 (where fuel composition is $\text{C}_x\text{H}_y\text{O}_z$ as measured for the fuel used.)

a) For M100 (100% methanol), CH_3OH , where $x = 1$, $y = 4$, and $z = 1$:
 $\text{DF} = 11.57 / [\text{CO}_{2e} + (\text{NMHC}_e + \text{CH}_{4e} + \text{CO}_e + \text{CH}_3\text{OH}_e + \text{HCHO}_e) * 10^{-4}]$

b) For M85 (85% methanol, 15% Indolene), $\text{CH}_{3.41} \text{O}_{0.72}$, where $x = 1$, $y = 3.41$, and $z = 0.72$:
 $\text{DF} = 12.02 / [\text{CO}_{2e} + (\text{NMHC}_e + \text{CH}_{4e} + \text{CO}_e + \text{CH}_3\text{OH}_e + \text{HCHO}_e) * 10^{-4}]$

5.4 Vehicles Operating on Fuels Containing Ethanol

$$5.4.1 \quad \text{NMHC}_e = \text{FID THC}_e - (r_{\text{CH}_4} * \text{CH}_{4e}) - (r_{\text{C}_2\text{H}_5\text{OH}} * \text{C}_2\text{H}_5\text{OH}_e)$$

NOTE: If NMHC_e is calculated to be less than zero, then $\text{NMHC}_e = 0$.

$$5.4.2 \quad \text{NMHC}_d = \text{FID THC}_d - (r_{\text{CH}_4} * \text{CH}_{4d}) - (r_{\text{C}_2\text{H}_5\text{OH}} * \text{C}_2\text{H}_5\text{OH}_d)$$

NOTE: If NMHC_d is calculated to be less than zero, then $\text{NMHC}_d = 0$.

$$5.4.3 \quad \text{CO}_e = (1 - (0.01 + 0.005 * \text{HCR}) * \text{CO}_{2e} - 0.000323 * R_a) * \text{CO}_{em}$$

NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e .

a) For E100 (100% ethanol), $\text{C}_2\text{H}_5\text{OH}$, where $\text{HCR} = 3$:

$$\text{CO}_e = (1 - 0.02500 * \text{CO}_{2e} - 0.000323 * R_a) * \text{CO}_{em}$$

$$100 * \frac{x}{x + y/2 + 3.76 * (x + y/4 - z/2)}$$

$$5.4.4 \quad \text{DF} = \frac{100 * \frac{x}{x + y/2 + 3.76 * (x + y/4 - z/2)}}{\text{CO}_{2e} + (\text{NMHC}_e + \text{CH}_{4e} + \text{CO}_e + \text{C}_2\text{H}_5\text{OH}_e + \text{HCHO}_e) * 10^{-4}}$$

(where fuel composition is $\text{C}_x\text{H}_y\text{O}_z$ as measured for the fuel used.)

a) For E100 (100% ethanol), $\text{C}_2\text{H}_5\text{OH}$, where $x = 1$, $y = 3$, and $z = 0.5$:

$$\text{DF} = 12.29 / [\text{CO}_{2e} + (\text{NMHC}_e + \text{CH}_{4e} + \text{CO}_e + \text{C}_2\text{H}_5\text{OH}_e + \text{HCHO}_e) * 10^{-4}]$$

5.5 All Vehicles

$$5.5.1 \quad \text{NMHC}_{\text{conc}} = \text{NMHC}_e - \text{NMHC}_d * [1 - (1 / \text{DF})]$$

NOTE: If $\text{NMHC}_{\text{conc}}$ is calculated to be less than zero, then $\text{NMHC}_{\text{conc}} = 0$.

$$5.5.2 \quad \text{NMHC}_{\text{mass}_n} = \text{NMHC}_{\text{conc}} * \text{NMHC}_{\text{dens}} * \text{VMIX} * 10^{-6}$$

6. TOTAL WEIGHTED NMHC MASS EMISSIONS

6.1 All Vehicles

$$6.1.1 \quad \text{NMHC}_{\text{wm}} = 0.43 * \frac{\text{NMHC}_{\text{mass}_1} + \text{NMHC}_{\text{mass}_2}}{D_{\text{phase}_1} + D_{\text{phase}_2}} + 0.57 * \frac{\text{NMHC}_{\text{mass}_3} + \text{NMHC}_{\text{mass}_2}}{D_{\text{phase}_3} + D_{\text{phase}_2}}$$

7. SAMPLE CALCULATIONS

7.1 Given the following data for a gasoline vehicle, calculate the weighted NMHC mass emission.

Test Phase	FID THC _e (ppmC)	FID THC _d (ppmC)	CH _{4e} (ppmC)	CH _{4d} (ppmC)	CO _{em} (ppm)	CO _{2e} (%)	VMIX (ft ³)	D _{phase n} (mile)	R _a (%)
1	41.8	8.6	7.53	5.27	147.2	1.19	2846	3.583	38
2	13.0	8.4	5.68	5.10	20.8	0.80	4856	3.848	38
3	15.4	8.9	6.16	5.20	36.7	1.04	2839	3.586	38

For Phase 1:

$$\begin{aligned}
 \text{NMHC}_e &= \text{FID THC}_e - (r_{\text{CH}_4} * \text{CH}_{4e}) \\
 &= 41.8 \text{ ppmC} - (1.04 * 7.53 \text{ ppmC}) \\
 &= 33.97 \text{ ppmC}
 \end{aligned}$$

$$\begin{aligned}
 \text{NMHC}_d &= \text{FID THC}_d - (r_{\text{CH}_4} * \text{CH}_{4d}) \\
 &= 8.6 \text{ ppmC} - (1.04 * 5.27 \text{ ppmC}) \\
 &= 3.12 \text{ ppmC}
 \end{aligned}$$

$$\begin{aligned}
 \text{CO}_e &= (1 - 0.01925 * \text{CO}_{2e} - 0.000323 * R_a) * \text{CO}_{em} \\
 \text{NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO}_{em} \text{ must be substituted directly for CO}_e.
 \end{aligned}$$

$$\begin{aligned}
 &= (1 - 0.01925 * 1.19\% - 0.000323 * 38\%) * 147.18 \text{ ppm} \\
 &= 142.0 \text{ ppm}
 \end{aligned}$$

$$\begin{aligned}
 \text{DF} &= 13.47 / [\text{CO}_{2e} + (\text{NMHC}_e + \text{CH}_{4e} + \text{CO}_e) * 10^{-4}] \\
 &= \frac{13.47}{1.19\% + (33.97 \text{ ppmC} + 7.53 \text{ ppmC} + 142.0 \text{ ppmC}) * 10^{-4}} \\
 &= 11.15
 \end{aligned}$$

$$\begin{aligned}
 \text{NMHC}_{\text{conc}} &= \text{NMHC}_e - \text{NMHC}_d * [1 - (1 / \text{DF})] \\
 &= 33.97 \text{ ppmC} - 3.12 \text{ ppmC} * [1 - (1 / 11.15)] \\
 &= 31.13 \text{ ppmC}
 \end{aligned}$$

$$\begin{aligned}
 \text{NMHC}_{\text{mass n}} &= \text{NMHC}_{\text{conc}} * \text{NMHC}_{\text{dens}} * \text{VMIX} * 10^{-6} \\
 &= 31.13 \text{ ppmC} * 16.33 \text{ g/ft}^3 * 2846 \text{ ft}^3 * 10^{-6}
 \end{aligned}$$

$$\text{NMHC}_{\text{mass 1}} = 1.45 \text{ g}$$

$$\begin{aligned} \text{Similarly, for Phase 2:} \quad \text{NMHC}_{\text{mass 2}} &= 0.33 \text{ g} \\ \text{and for Phase 3:} \quad \text{NMHC}_{\text{mass 3}} &= 0.27 \text{ g} \end{aligned}$$

Therefore,

$$\begin{aligned} \text{NMHC}_{\text{wm}} &= 0.43 * \frac{\text{NMHC}_{\text{mass 1}} + \text{NMHC}_{\text{mass 2}}}{D_{\text{phase 1}} + D_{\text{phase 2}}} + 0.57 * \frac{\text{NMHC}_{\text{mass 3}} + \text{NMHC}_{\text{mass 2}}}{D_{\text{phase 3}} + D_{\text{phase 2}}} \\ &= 0.43 * \frac{1.45 \text{ g} + 0.33 \text{ g}}{3.583 \text{ mile} + 3.848 \text{ mile}} + 0.57 * \frac{0.27 \text{ g} + 0.33 \text{ g}}{3.586 \text{ mile} + 3.848 \text{ mile}} \end{aligned}$$

$$\text{NMHC}_{\text{wm}} = 0.15 \text{ g/mile}$$

7.2 Given the following data for a vehicle operating on 85% methanol and 15% gasoline (M85), calculate the weighted NMHC mass emission.

Test Phase	FID THC _e (ppmC)	FID THC _d (ppmC)	CH _{4e} (ppmC)	CH _{4d} (ppmC)	CH _{3OH_e} (ppm)	CO _{em} (ppm)	CO _{2e} (%)	VMIX (ft ³)	D _{phase n} (mile)	R _a (%)	HCHO _e (ppm)
1	88.5	5.5	17.76	2.82	72.9	303.2	1.28	2832	3.570	32	0.96
2	14.5	7.0	8.01	2.82	5.1	9.7	0.83	4827	3.850	32	0.10
3	21.8	7.7	10.13	2.93	7.4	18.2	1.13	2825	3.586	32	0.12

[For this example, CH_{3OH_d} was assumed to be 0.0 ppmC for all three background bag samples.]

For Phase 1:

$$\begin{aligned} \text{NMHC}_e &= \text{FID THC}_e - (r_{\text{CH}_4} * \text{CH}_{4e}) - (r_{\text{CH}_3\text{OH}} * \text{CH}_3\text{OH}_e) \\ &= 88.5 \text{ ppmC} - (1.04 * 17.76 \text{ ppmC}) - (0.66 * 72.9 \text{ ppmC}) \\ &= 21.92 \text{ ppmC} \end{aligned}$$

$$\begin{aligned} \text{NMHC}_d &= \text{FID THC}_d - (r_{\text{CH}_4} * \text{CH}_{4d}) - (r_{\text{CH}_3\text{OH}} * \text{CH}_3\text{OH}_d) \\ &= 5.5 \text{ ppmC} - (1.04 * 2.82 \text{ ppmC}) - (0.66 * 0.0 \text{ ppmC}) \\ &= 2.57 \text{ ppmC} \end{aligned}$$

$$CO_e = (1 - 0.02705 * CO_{2e} - 0.000323 * R_a) * CO_{em}$$

NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e .

$$= (1 - 0.02705 * 1.28\% - 0.000323 * 32\%) * 303.2 \text{ ppm}$$

$$= 289.6 \text{ ppm}$$

$$DF = 12.02 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e + CH_3OH_e + HCHO_e) * 10^{-4}]$$

$$= \frac{12.02}{1.28\% + (21.92\text{ppmC} + 17.76\text{ppmC} + 289.6 \text{ ppmC} + 72.9\text{ppmC} + 0.96\text{ppm}) * 10^{-4}}$$

$$= 9.10$$

$$NMHC_{conc} = NMHC_e - NMHC_d * [1 - (1 / DF)]$$

$$= 21.92 \text{ ppmC} - 2.57 \text{ ppmC} * [1 - (1 / 9.10)]$$

$$= 19.63 \text{ ppmC}$$

$$NMHC_{mass \ n} = NMHC_{conc} * NMHC_{dens} * VMIX * 10^{-6}$$

$$NMHC_{mass \ 1} = 0.91 \text{ g}$$

$$\text{Similarly, Phase 2: } NMHC_{mass \ 2} = 0.0 \text{ g}$$

$$\text{and for Phase 3: } NMHC_{mass \ 3} = 0.10 \text{ g}$$

Therefore,

$$NMHC_{wm} = 0.43 * \frac{NMHC_{mass \ 1} + NMHC_{mass \ 2}}{D_{phase \ 1} + D_{phase \ 2}} + 0.57 * \frac{NMHC_{mass \ 3} + NMHC_{mass \ 2}}{D_{phase \ 3} + D_{phase \ 2}}$$

$$= 0.43 * \frac{0.91 \text{ g} + 0.00 \text{ g}}{3.570 \text{ mile} + 3.850 \text{ mile}} + 0.57 * \frac{0.10 \text{ g} + 0.0 \text{ g}}{3.586 \text{ mile} + 3.850 \text{ mile}}$$

$$NMHC_{wm} = 0.06 \text{ g/mile}$$

8. ~~DEFINITIONS~~

~~CH_3OH_d — the methanol concentration in the dilution air as determined from the dilution air methanol sample using the procedure specified in Method No. 1001, ppmC.~~

~~CH_3OH_e — the methanol concentration in the dilute exhaust as determined from the dilute exhaust methanol sample using the procedure specified in Method No. 1001, ppmC.~~

~~CH_{4d} — the methane concentration in the dilution air, ppmC.~~

CH_{4e} = ~~the methane concentration in the dilute exhaust, ppmC.~~

$C_2H_5OH_d$ = ~~the ethanol concentration in the dilution air as determined from the dilution air ethanol sample using the procedure specified in Method No. 1001, ppmC.~~

$C_2H_5OH_e$ = ~~the ethanol concentration in the dilute exhaust as determined from the dilute exhaust ethanol sample using the procedure specified in Method No. 1001, ppmC.~~

CO_e = ~~the carbon monoxide concentration in the dilute exhaust corrected for carbon dioxide and water removal, ppm.~~

CO_{em} = ~~the carbon monoxide concentration in the dilute exhaust uncorrected for carbon dioxide and water removal, ppm.~~

CO_{2e} = ~~the carbon dioxide concentration in the dilute exhaust, %.~~

$D_{phase\ n}$ = ~~the distance driven by the test vehicle on a chassis dynamometer during test phase n (where n is either 1, 2, or 3), mile.~~

DF = ~~dilution factor.~~

FID-THC_d = ~~the total hydrocarbon concentration including methane and methanol (for methanol-fueled engines) or ethanol (for ethanol-fueled engines) in the dilution air as measured by the FID, ppmC.~~

FID-THC_e = ~~the total hydrocarbon concentration including methane and methanol (for methanol-fueled engines) or ethanol (for ethanol-fueled engines) in the dilute exhaust as measured by the FID, ppmC.~~

HCHO_e = ~~the formaldehyde concentration in the dilute exhaust as determined from the dilute exhaust carbonyl sample using the procedure specified in Method No. 1004, ppm.~~

HCR = ~~the hydrogen-to-carbon ratio for the fuel used.~~

NMHC_{conc} = ~~the non-methane hydrocarbon concentration in the dilute exhaust corrected for background, ppmC.~~

NMHC_d = ~~the non-methane hydrocarbon concentration in the dilution air corrected for methane and alcohol removal, ppmC.~~

NMHC_{dens} = ~~the mass per unit volume of non-methane hydrocarbon corrected to standard conditions (16.33 g/ft³ at 293.16° K and 760 mm Hg assuming a C:H ratio of 1:1.85 and 17.28 g/ft³ for LPG at 293.16° K and 760 mm Hg), g/ft³.~~

NMHC_e = ~~the non-methane hydrocarbon concentration in the dilute exhaust corrected for methane and alcohol removal, ppmC.~~

~~NMHC_{mass n} = the mass emission of non-methane hydrocarbon per test phase n (where n is either 1, 2, or 3), g.~~

~~NMHC_{wtm} = the total weighted mass of non-methane hydrocarbon per mile for all three phases of the FTP, g/mile.~~

~~R_a = the relative humidity of the ambient air, percent.~~

~~f_{CH₃OH} = the FID response factor to methanol (see CFR 40, 86.121-90(c)).~~

~~f_{CH₄} = the FID response factor to methane (see section 4).~~

~~f_{C₂H₅OH} = the FID response factor to ethanol (same procedure for methanol response factor, see CFR 40, 86.121-90(c)).~~

~~VMIX = the total dilute exhaust volume measured per test phase and corrected to standard conditions (293.16° K and 760 mm Hg), ft³.~~

~~9. REFERENCES~~

- ~~(1) Code of Federal Regulations, Title 40, Part 86, Subpart B~~
- ~~(2) SAE J254, "Instrumentation and Techniques for Exhaust Gas Emissions Measurement"~~
- ~~(3) SAE J1094a, "Constant Volume Sampler System for Exhaust Emissions Measurement"~~
- ~~(4) SAE 770141, "Optimization of a Flame Ionization Detector for Determination of Hydrocarbon in Diluted Automotive Exhausts". G.D. Reschke, Vehicle Emissions Laboratory, General Motors Proving Ground~~
- ~~(5) SAE J1154, "Methane Measurement Using Gas Chromatography", (revised December 1991)~~

Part C

DETERMINATION OF ALCOHOLS IN AUTOMOTIVE SOURCE SAMPLES BY GAS CHROMATOGRAPHY

METHOD NO. 1001

1. INTRODUCTION

- 1.1 This document describes a method of sampling and analyzing automotive exhaust for alcohols in the range of 8 to 1200 ~~micrograms~~ (µg) per 15 ~~milliliters~~ (mL) of solution. The "target" alcohols which shall be analyzed and reported by this method are methanol and ethanol. These alcohols, when present in concentrations above the LOD, shall be reported.
- 1.2 This procedure is based on a method developed by the U. S. Environmental Protection Agency, (U.S. EPA) [Ref 9-1 6] which involves flowing diluted engine exhaust through deionized or purified water contained in glass impingers and analyzing this solution by gas chromatography (GC).
- 1.3 All definitions and abbreviations are contained in Appendix 2 of these test procedures.

2. METHOD SUMMARY

- 2.1 The samples are received by the laboratory in impingers. Compound separation and analysis are performed using a GC. The sample is injected into the GC by means of a liquid autosampler. Separation of the sample mixture into its components ~~constituents~~ is performed by using a temperature-programmed capillary column ~~operated with a temperature gradient~~. A ~~flame ionization detector (FID)~~ is used for alcohol detection and quantification.
- 2.2 The computerized GC data system identifies the alcohol associated with each ~~of the~~ peaks. The alcohol concentrations are determined by integrating the peak areas and using response factors determined ~~with~~ from external standards.

3. INTERFERENCES AND LIMITATIONS

- 3.1 An ~~interference~~ interferent is any component present in the sample with a retention time similar to that of ~~any the~~ target alcohols described in this method. To reduce interference error, proof of chemical identity may require ~~performance of~~ periodic confirmations using an alternate method and/or instrumentation, e.g., ~~gas chromatograph/mass spectrometer (GC/MS)~~.
- 3.2 The concentration of the alcohols in the range of interest is stable for up to six days as long as the samples are sealed and refrigerated at a temperature below 40°F.

4. INSTRUMENTATION AND APPARATUS

- 4.1 For each mode of the CVS test, two sampling impingers, each containing a known amount of deionized or purified water (e.g. 15 mL for this procedure), are used to contain the sample.
- 4.1.1 A temperature-programmable GC, equipped with a DB-Wax Megabore column (30 ~~meter~~ (m), 0.53 ~~millimeter~~ (mm) ID, 1.0 ~~micron~~ (μ) film thickness) and FID is used. Other columns may be used, provided the alternate(s) can be demonstrated to be equivalent or better with respect to precision, accuracy and resolution of all the target alcohols.
- 4.1.2 A liquid autosampler is required.
- 4.1.3 A PC-controlled data acquisition system for ~~quantitation~~ quantifying of peak areas is required.

5. REAGENTS AND MATERIALS

- 5.1 Methanol shall have a purity of 99.9 percent, or be high performance liquid chromatography grade, EM Science or equivalent.
- 5.2 Ethanol shall be absolute, ACS reagent grade.
- 5.3 ~~American Standards for Testing Materials~~ ASTM Type I purified or Type II deionized water shall be used.
- 5.4 A stock solution is prepared gravimetrically or volumetrically by diluting methanol and ethanol with deionized or purified water, e.g., for this method the stock solution contains ~~is approximately~~ ± 10 mg/mL percent by volume of each target alcohol.
- 5.4.1 A **calibration standard** within at the expected concentration range of the samples is prepared by successive dilutions of the stock solution with deionized or purified water, e.g., 50 ~~parts per million (ppm)~~ μg/mL ~~volume to volume (v/v)~~ is typical.
- 5.4.2 A **control standard** containing all target alcohols is prepared by successive dilutions of a stock solution different from that of Section 5.4.1. This standard, at an approximate concentration of the samples, is used to monitor the precision of the analysis of ~~update control charts for~~ each target alcohol.
- 5.4.3 All standards should be refrigerated at ~~less than~~ a temperature below 40° F during storage.
- 5.5 Gas requirements.
- 5.5.1 Air shall be "Zero" grade. "Ultra-zero" grade may be required to achieve the LOD required by Section 8.8.
- 5.5.2 Nitrogen shall have a minimum purity of 99.998 percent.
- 5.5.3 Helium shall have a minimum purity of 99.995 percent.
- 5.5.4 Hydrogen shall have a minimum purity of 99.995 percent.

6. PROCEDURE

- 6.1 Each of the graduated ~~fritted~~ sampling impingers is filled with 15 mL of deionized or purified water.
- 6.2 The impingers are placed in an ice bath during the sample collection.
- 6.3 After sampling, ~~the impingers are allowed to warm to room temperature and the solution contained in each impinger is transferred to a vial and sealed.~~
- 6.3.1 Samples ~~should~~ shall be refrigerated (at a temperature below 40°F or lower) if immediate analysis is not feasible, or if reanalysis at a later date may be required.
- 6.4 One microliter aliquots of unmodified samples are injected via autosampler into a GC. Suggested standard operating conditions for the GC are: ~~configured as follows:~~
- Column: DB-~~w~~Wax, 30 m, 0.53 mm ID, 1.0μ film thickness
- Carrier gas flow: Helium at 5 ~~milliliters per minute~~ (mL/min)
- Make-up gas flow: Nitrogen at 25 mL/min
- Detector: FID, Hydrogen at 30 mL/min and Air at 300 mL/min
- Injector: Packed column injector with Megabore adapter insert; on-column injection
- Column Temperature: 50°C (1 min), 50°C to 70°C (5°C/min), 70°C to 110°C (15°C/min), 110°C (4 min)
- Data system: PC-based data acquisition system
- 6.4.1 One calibration standard, one control standard, and one deionized or purified water blank are analyzed daily at the beginning of each set of samples.
- 6.4.2 A replicate analysis is performed at least once per 24 hour period.
- 6.4.3 The control standard is analyzed ~~performed~~ at least once per 24 hour period.
- 6.4.4 For Samples containing compounds having concentrations above the documented range of instrument linearity, ~~the sample~~ must be diluted and reanalyzed.
- 6.4.5 The peak integrations are corrected as necessary in the data system. Any misplaced baseline segments are corrected in the reconstructed chromatogram.
- 6.4.6 The peak identifications provided by the computer are checked and corrected if necessary.
- 6.4.7 The target alcohol peaks at or above the ~~maximum allowable limit of detection (LOD)~~ are reported (Section 8.8). ~~At the laboratory's discretion, peaks at or above the LOD calculated in section 8.8 may be reported. The calculated LOD must be lower than the maximum allowable LOD.~~

7. CALCULATIONS

- 7.1 The concentration of each target alcohol, in μg/mL, is determined by the following calculation that compares the sample peak area with that of an external standard:

$$\text{Concentration } (\mu\text{g/mL})_{\text{sample}} = \text{Peak Area}_{\text{sample}} \times \text{Response Factor}$$

where the response factor (RF) is calculated during the calibration by:

$$RF = \frac{\text{Concentration}_{\text{standard}} (\mu\text{g/mL})}{\text{Peak Area}_{\text{standard}}}$$

7.2 This concentration is then used to calculate the total amount of alcohol in each impinger:

$$\text{Mass } (\mu\text{g}) = \text{Concentration } (\mu\text{g/mL}) \times \text{Impinger volume (mL)}$$

7.3 An internal standard method may also be used.

8. **QUALITY CONTROL**

8.1 Calibration and control standards are prepared at least every six months and analyzed daily.

8.2 Blank Run. A deionized or purified water blank run is performed before running the calibration standard. All target alcohol concentrations from the blank analysis must be below the LOD before the analysis may proceed.

8.3 Calibration Run. One run of the calibration standard is performed daily to generate the response calibration factor needed for ~~quantitating~~ quantifying sample analyses.

8.4 Control Standard Run. One run of the quality control standard is performed after the calibration run. Measurements of all target alcohols in the control standard must fall within the control limits before sample analysis may proceed. To meet this requirement, it may be necessary to inspect and repair the GC, and rerun the calibration and/or control standards.

8.5 Control Charts. ~~A q~~Quality control chart(s) ~~is are~~ maintained for each analyte ~~in of~~ the control ~~standard sample~~. The control charts, used on a daily basis, establishes that the method is "in ~~statistical-~~ control". The following describes how to construct a typical control chart:

1. Obtain at least 20 daily control standard sample results;
2. Calculate the ~~average~~ control standard sample mean concentration and standard deviation(s) for the target analyte(s); and
3. Create a control chart for the target analyte(s) by placing the concentration on the Y-axis and the date on the X-axis. Establish ~~Draw~~ an upper warning limit and a lower warning limit at two standard deviations (2s) above and below the average concentration. Establish ~~Draw~~ an upper control limit and a lower control limit at three standard deviations (3s) above and below the average concentration.

~~The control sample must be "in-control" for~~ The measured concentrations of all target analytes contained in the control standard must be within the control limits ("in-control") for the sample results to be considered acceptable. A control standard sample measurement is considered to be "out-of-control" when the analyzed value exceeds the 3s limit, or two successive control standard sample measurements of the same analyte exceed the 2s limit.

8.6 Duplicates. A duplicate analysis of one sample is performed at least once a day. The relative percent difference (RPD) is calculated for each duplicate run:

$$\text{RPD}(\%) = \frac{\text{Difference between duplicate and original measurements}}{\text{Average of duplicate and original measurements}} \times 100$$

For each compound, the allowable RPD depends on the average concentration level for the duplicate runs, as shown in the following table:

<u>Average Measurement for Duplicate Runs</u>		<u>Allowable RPD (%)</u>
1 to 10	times LOD	100
10 to 20	" "	30
20 to 50	" "	20
Greater than 50	" "	15

If the results of the duplicate analyses do not meet these criteria for all target alcohols, the sample must be reanalyzed. If the criteria are still not met, all sample results for the day from this instrument must be deleted and the samples reanalyzed.

8.7 Linearity. A multipoint calibration to confirm check for instrument linearity is performed for all target alcohols for new instruments, after making instrument modifications which can affect linearity, and at least once every year ~~every six months~~. The multipoint calibration consists of at least five concentration or mass loading levels, each above the LOD, ~~evenly~~ distributed over the range of expected sample concentration linearity of the instrument. Each concentration level is measured at least twice. A linear regression analysis is performed using concentration and area counts to determine the regression correlation coefficient (r). The r must be greater than 0.995 to be considered sufficiently linear for one point calibrations.

8.8 Limit of Detection. The LOD limit of detection for the target alcohols must be determined for new instruments, after making instrument modifications which can affect the LOD and at least once every year. ~~every six months~~. To make the calculations, it is necessary to perform a multipoint calibration consisting of at least four "low" concentration levels, each above the expected LOD. A linear regression is performed on the data. The LOD must be calculated using the following equation [Ref. 7] ~~(Ref 9.2)~~:

$$\text{LOD} = \frac{|b| + (t \times s)}{m}$$

$$\text{LOD} = |A| + 3.3(S)$$

where ~~each term in the equation is expressed in concentration units, and |A| is the absolute value of the least squares X-intercept calculated from the multipoint data. S~~ |b| is the absolute value of the y-intercept, m is the slope of the linear regression, s is the standard deviation of at least five replicate determinations of the lowest concentration standard, and t is the t-factor for 99 percent confidence for a one-sided normal (Gaussian) distribution. The number of degrees of freedom is equal to the number of replicates, minus one. An abbreviated t-table is:

<u>Degrees of Freedom</u>	<u>t-value</u>
<u>4</u>	<u>3.7</u>
<u>5</u>	<u>3.4</u>

6
7

3.1
3.0

~~At least three replicates are required. The lowest standard must be of a concentration of at one to five times the estimated LOD detection limit. If data is not available in the concentration range near the detection limit, \underline{S} may be estimated by:~~

$$\underline{S} = \text{RSD} \times \underline{A}$$

~~RSD is the relative standard deviation of the lowest standard analyzed.~~

~~An example of typical LODs is given in the table below:~~

CAS Nos.	COMPOUND	LOD (ug/ml)
00067-56-1	methanol	0.24
00064-17-5	ethanol	0.17

8.8.1 The maximum allowable LOD for each alcohol is 0.50 µg/mL. The calculated laboratory LOD must be equal to or lower than the maximum allowable LOD. All peaks identified as target compounds that are equal to or exceed the maximum allowable LOD must be reported. If the calculated laboratory LOD is less than the maximum allowable LOD, the laboratory may choose to set its reporting limit at either the maximum allowable LOD or the calculated laboratory LOD.

8.8.2. For the purpose of calculating the total mass of all species, the concentrations of the compounds below the LOD are considered to be zero.

~~9. REFERENCES~~

9.1 ~~U.S. Environmental Protection Agency, Characterization of Exhaust Emissions from Methanol and Gasoline Fueled Automobiles, EPA 460/3-82-004.~~

9.2 ~~U.S. Environmental Protection Agency, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, (Method T03-15) EPA-600/4-89-017 Research Triangle Park, North Carolina, June, 1989.~~

Part D

DETERMINATION OF C₂ TO C₅ HYDROCARBONS IN AUTOMOTIVE SOURCE SAMPLES BY GAS CHROMATOGRAPHY

METHOD NO. 1002

1. INTRODUCTION

- 1.1 This document describes a method of analyzing, by gas chromatography, C₂ to C₅ hydrocarbons (light-end hydrocarbons) in the range of ~~parts per billion carbon (ppbC)~~ from automotive source samples. This method does not include sample collection procedures [Ref. 8] (~~Ref 9.1~~). The "target" hydrocarbons which shall be analyzed and reported by this method and Method 1003 are listed in Attachment Appendix 1. All compounds on this list, when present in concentrations above the LOD, shall be measured and reported ("targeted") by either Method 1002 or Method 1003. Each laboratory should divide the list into light-end (Method 1002) and mid-range (Method 1003) hydrocarbons in the manner which best suits the laboratory instrumentation. All compounds on the list not targeted by Method 1002 must be targeted by Method 1003. ~~More compounds may be measured than those on the target list.~~
- 1.2 All definitions and abbreviations are contained in Appendix 2 of these test procedures.

2. METHOD SUMMARY

- 2.1 This is a ~~rapid~~ method intended for routine analysis.
- 2.2 The samples are received by the laboratory in Tedlar bags, which are sub-sampled into a ~~gas chromatograph (GC)~~ for separation and ~~analyses~~ analysis.
- 2.3 The gas chromatographic analysis is performed on a packed column operated isothermally at 35°C, or an Alumina (Al₂O₃) ~~Porous Layer Open Tubular (PLOT)~~ column temperature programmed from 0°C to 200°C. ~~An flame ionization detector (FID)~~ is used for detection and quantification.
- 2.4 The sample is injected into the GC by means of gas sampling valves. Separation of the sample hydrocarbon mixture into its components ~~constituents~~ takes place in the chromatographic column. The chromatographic column and the corresponding operating parameters described in this method normally provide complete resolution of most target compounds.
- 2.5 The computerized GC data acquisition system identifies the hydrocarbons associated with each ~~of the peaks~~. The hydrocarbon concentrations are determined by integrating the peak areas and using response calibration factors determined from ~~with~~ NIST-traceable standards.

3. INTERFERENCES AND LIMITATIONS

- 3.1 An ~~interference~~ interferent is any component present in the sample with a retention time very similar to that of ~~any the~~ target hydrocarbons described in this method. To reduce interference error, proof of chemical identity may require ~~performance of~~ periodic confirmations using an alternate method and/or instrumentation, e.g., ~~gas chromatograph/mass spectrometer (GC/MS), photoionization detector (PID),~~ different column, etc.
- 3.2 To maximize sample integrity, sample bags should not leak or be exposed to bright light or excessive heat. Sampling bags must be shielded from direct sunlight to avoid reactions occurring due to reactive hydrocarbons. The compound 1,3-butadiene, most of which is in CVS bag no. 1, is unstable. Therefore all CVS bag no. 1 samples must be analyzed within 8 ± hours; CVS bag no. 2, CVS bag no. 3, and background samples must be analyzed within 24 hours, although analysis within 8 hours is recommended.

4. INSTRUMENTS AND APPARATUS

- 4.1 Tedlar bags, 2 mil in thickness, nominally 5 to 10 liters in capacity and equipped with quick-connect fittings, are used to contain the samples.
- 4.2 For manual sub-sampling into a GC, a ground glass syringe is used to transfer gaseous samples from Tedlar bags to the GC sample inlet. For automated systems, a sample loop is used to transfer gaseous samples from the Tedlar bag to the sample inlet of the GC. Sample aliquot size is chosen based on considerations of instrument sensitivity and/or linearity.
- 4.3 A temperature-programmable GC equipped with a gas sampling valve system, a FID, and accessories is required.
- 4.4 A stainless steel column [6 ~~feet~~ (ft) x 1/8 ~~inch~~ (in)] packed with phenylisocyanate Durapak 80/100 mesh is used. ~~An Al₂O₃ Alumina PLOT column (50 -60 m x 0.32 mm) may also be used. has been shown to be equivalent~~ A wax precolumn is recommended to prevent water damage to the PLOT column. Other columns may be used, provided the alternate(s) can be demonstrated to be equivalent or better with respect to precision, accuracy and resolution of all the target hydrocarbons.
- 4.5 A sample trap capable of being cryogenically cooled may be used.
- 4.56 An electronic integrator for quantitation of peak areas is required. If the data acquisition system cannot record the chromatogram, an analog recorder is also required.

5. REAGENTS AND MATERIALS

- 5.1 Helium shall have a minimum purity of 99.995 percent. Higher purity helium may be required to achieve the LOD required by Section 8.7.1.
- 5.2 Hydrogen shall have a minimum purity of 99.995 percent.

- 5.3 Air shall be "Zero" grade. "Ultra-zero" grade may be required to achieve the LOD required by Section 8.7.1.
- 5.4 Nitrogen shall have a minimum purity of 99.998 percent.
- 5.5 **Calibration Standard** - The quantitative calibration standard for all target hydrocarbons shall be propane at a concentration level between 0.25 and 1 ppm-mole and within the calculated linearity of the method (see section 8.6). This propane standard must be traceable to a NIST-certified SRM ~~to a Standard Reference Material (SRM) certified for propane by the National Institute of Standards and Technology (NIST).~~ NIST traceable means that the standard has been compared with not more than one intermediate standard to a NIST-certified SRM. A comparison between a SRM and a candidate standard will yield a secondary NIST traceable standard, while a comparison between a secondary NIST traceable standard and a candidate standard will yield a tertiary NIST traceable standard. A NIST SRM propane standard, secondary NIST traceable propane standard, or tertiary NIST traceable propane standard is required for calibration of M~~method~~ 1002 or 1003.

~~The minimum requirements for the manufacture and use of a secondary or tertiary NIST traceable propane standard shall be the following: 1) the standard must be packaged in aluminum cylinders which have been precleaned and passivated, 2) a gas chromatograph shall be used to compare the candidate cylinders with the NIST traceable standard using either direct or interpolation comparison. (In the direct comparison, the analyte concentration for the candidate standard may not differ more than 10 percent from the analyte concentration of the NIST traceable standard; while in the interpolation comparison, the analyte concentration of a candidate standard is bracketed between the analyte concentrations of the NIST SRM standards.); 3) analytes and balance gases in secondary candidate cylinders must be the same composition as the NIST SRM propane standards used in an interpolation comparison procedure, 4) hydrocarbon analytes (except propane) and balance gases may differ in secondary candidate cylinders from the NIST SRM propane standard used in a direct comparison procedure if there are no interferences with the propane measurement or stability, 5) comparison between a secondary and tertiary standard must be direct, 6) all candidate cylinders must be analyzed a minimum of 4 times and stated uncertainties must be determined for all secondary and tertiary standard analytes, and 7) gas in the cylinder cannot be used when the pressure of the cylinder falls below 300 pounds per square inch.~~

~~It is recommended that either the laboratory or standard supplier(s) for the laboratory certify the secondary standards through the NIST Traceable Reference Material program or obtain Research Gas Material/Mixtures of propane standards from NIST for use as secondary standards.~~

- 5.6 **Control Standard** - A quality control standard, containing at least ethene, propane, n-butane, and 2-methylpropene with a concentration between 0.2 and 1 ~~parts per million carbon (ppmC)~~ based on a propane standard, is used for the following quality control purposes:
1. Daily update of control charts, and
 2. Daily determination of marker retention time windows.

~~The control standard(s) must have concentrations verified against a NIST-traceable propane standard (See Section 5.5 for definition of NIST-traceable) when used for either LOD determinations or linearity checks. This verification can be performed at the laboratory conducting the sample analysis.~~

- 5.7 A high concentration standard (higher than the calibration standard), containing the target hydrocarbons listed in Section 5.6 is used ~~semi-annually~~ for linearity determinations. The high ~~concentration~~ calibration standard must have concentrations verified against a NIST-traceable propane standard (see Section 5.5 for the definition of NIST-traceable). This verification can be performed at the laboratory performing the analysis.
- 5.8 Liquid nitrogen may be required ~~is used~~ to cool the cryogenic sample trap and column oven where applicable.

6. **PROCEDURE**

- 6.1 The gaseous sample is analyzed for the target hydrocarbons C₂ through C₅.
- 6.2 Suggested standard operating conditions for the gas chromatograph are:

6.2.1 Packed Column:

Helium carrier gas flow:	50 milliliter/minute (mL/min) (packed column)
Hydrogen gas flow:	32 mL/min
Air flow:	300 mL/min
Sample valve temperature:	ambient
Heating bath temperature:	60° - 80° C
Injector temperature:	35° C (packed column)
Column temperature:	35° C (isothermal) (packed column)
	0° C to 200° C (temperature program) (AI PLOT Column)
Detector temperature:	200 to 250 ° C

6.2.2 PLOT Column:

<u>Helium carrier gas velocity:</u>	<u>30 cm/sec at 200° C</u>
<u>Nitrogen make-up gas flow:</u>	<u>sufficient such that the total flow of helium plus nitrogen is</u>
	<u>30 mL/min</u>
<u>Hydrogen gas flow:</u>	<u>30 mL/min</u>
<u>Air flow:</u>	<u>300 mL/min</u>
<u>Sample valve temperature:</u>	<u>150° C (PLOT column)</u>
<u>Column temperature:</u>	<u>0° C (hold 7 min), 10° C/min to 200° C (hold 15 min)</u>
<u>Detector temperature:</u>	<u>250° C</u>

- 6.3 For automated systems, connect the samples to the GC and begin the analytical process.
- 6.4 Introduce the sample into the carrier gas stream through the injection valve.
- 6.4 ~~For automated systems, connect the samples to the GC and begin the analytical process.~~

- 6.5 Each separated component exits from the column into the FID where a response is generated.
- 6.6 Concentrations of hydrocarbons are calculated by an electronic integrator device, which has been calibrated using a NIST-traceable propane calibration standard.
- 6.7 For compounds having concentrations above the documented range of instrument linearity, a smaller aliquot must be taken (for manual systems, a smaller syringe or smaller loop; for automated systems, a smaller loop).
- 6.8 The peak integrations are corrected as necessary in the data system. Any misplaced baseline segments are corrected in the reconstructed chromatogram.
- 6.9 The peak identifications provided by the computer are checked and corrected if necessary.
- 6.10 ~~All The peaks areas of identified as target compounds (Appendix 1) at or above the maximum allowable LOD are reported (Section 8.7). At the laboratory's discretion, peaks at or above the LOD calculated in section 8.7 may be reported. The calculated LOD must be lower than the maximum allowable LOD.~~
- 6.11 Target compounds which coelute are reported as the major component, as determined by the analysis of several samples by GC/MS or other methods. An exception to this is m- and p-xylene, where GC/MS data and fuel profiles are used to determine the relative contribution of each component to the peak. This method was used to determine the m- and p-xylene MIR value given in Appendix 1.
- ~~6.11 The maximum retention time in this analysis is typically about 15-30 mins.~~
- 6.12 After each run, the packed column is back-flushed with helium while the oven temperature is raised and maintained at 60°C for 15 mins, or as required to flush the column.
- 6.13 The ~~At~~ Alumina PLOT column is programmed to 200°C to assure all compounds are eluted before the next run.
- 6.134 Before the next run, sufficient time (~~typically 15 mins~~) is allowed after back-flush of the packed column to re-establish the required temperature of the column.
- ~~6.14 The total run time is typically about 45-60 mins.~~

7. CALCULATIONS

- 7.1 The target hydrocarbon concentrations, in ppbC, are calculated by the data system using propane as an external standard.

$$\text{Concentration}_{\text{sample}} (\text{ppbC}) = \text{Peak Area}_{\text{sample}} \times \text{Response Factor}$$

where the response factor (RF) is calculated during daily calibration by:

$$RF = \frac{\text{Concentration of NIST-traceable propane standard, ppbC}}{\text{Area of propane peak}}$$

8. QUALITY CONTROL

- 8.1 Blank Run. A blank (pure nitrogen or helium) is run once daily before running the calibration standard, control standard, and samples. All target hydrocarbon concentrations from the blank analysis must be below the LOD before the analysis may proceed. As an alternative to a daily blank run, a daily partial blank check in tandem with a weekly blank run may be used. A partial blank check is where the calibration standard, consisting of only propane and make-up gas (all organic compounds except methane and propane are below 2 percent of the propane standard concentration), is run daily and is checked for contamination except in the propane region of the chromatograph. The weekly blank run will provide a check on contamination in the propane region of the chromatograph.
- 8.2 Calibration Run. One run of the calibration standard is performed per day to generate the response calibration factor needed for ~~quantitating~~ quantifying sample analyses.
- 8.3 Control Standard Run. One run of the quality control standard is performed daily. Measurements of all compounds in the control standard must fall within the control limits before sample analysis may proceed. To meet this requirement, it may be necessary to inspect and repair the GC, and rerun the calibration and/or control standards.
- 8.4 Control Charts. ~~A quality control chart(s) are~~ is maintained for each component of the control ~~standard sample~~. The control charts, used on a daily basis, establishes that the method is "in-
"statistical control." The following describes how to construct a typical control chart:
1. Obtain at least 20 daily control ~~standard sample~~ results;
 2. Calculate the ~~average~~ control ~~standard sample mean~~ concentration and standard deviation(s) for ~~the each~~ target hydrocarbon; and
 3. Create a control chart for ~~the each~~ target hydrocarbon by placing the concentration on the Y-axis and the date on the X-axis. Establish an upper warning limit and a lower warning limit at two standard deviations (2s) above and below the average concentration. Establish an upper control limit and a lower control limit at three standard deviations (3s) above and below the average concentration.
- ~~The control sample must be "in-control" for~~ The measured concentrations of all target hydrocarbons contained listed in the control standard sample must be within the control limits ("in-control") for the sample results to be considered acceptable. A control standard sample measurement is considered to be "out-of-control" when the analyzed value of the sample measurement exceeds the 3s limit, or two successive control standard sample measurements of the same analyte exceed the 2s limit.
- 8.5 Duplicates. A duplicate analysis of one sample is performed at least once a day. The relative percent difference (RPD) is calculated for each duplicate run:

$$\text{RPD (\%)} = \frac{\text{Difference between duplicate and original measurements}}{\text{Average of duplicate and original measurements}} \times 100$$

For each compound in the control standard, the allowable RPD depends on the average concentration level for the duplicate runs, as shown in the following table:

<u>Average Measurement for the Duplicate Runs</u>			<u>Allowable RPD (%)</u>
1 to 10	times	LOD	100
10 to 20	"	"	30
20 to 50	"	"	20
Greater than 50	"	"	15

If the results of the duplicate analyses do not meet these criteria for all target hydrocarbons in the control standard, the sample must be reanalyzed. If the criteria are still not met, all sample results for the day from this instrument must be deleted and the samples reanalyzed.

8.6 Linearity. A multipoint calibration to confirm ~~check for~~ instrument linearity is performed for the target hydrocarbons in the control standard for new instruments, after making instrument modifications which can affect linearity, and at least once every year ~~six months~~ unless a daily check of the instrument response indicates that the linearity has not changed. To monitor the instrument response, a quality control chart is constructed, as specified in section 8.4, except using calibration standard area counts rather than control standard concentrations. When the standard area counts are out-of-control, corrective action(s) must be taken before analysis may proceed. The multipoint calibration consists of at least five concentration or mass loading levels (using smaller or larger volume sample sizes of existing standards is acceptable), each above the LOD, ~~evenly~~ distributed over the range of expected sample concentration ~~linearity of the instrument~~. Each concentration level is measured at least twice. A linear regression analysis is performed using concentration and average area counts to determine the regression correlation coefficient (r). The r must be greater than 0.995 to be considered sufficiently linear for one-point calibrations.

8.7 Limit of Detection. The ~~limit of detection~~ LOD for the target hydrocarbons in the control standard must be determined at least once every year ~~six months~~ unless a daily check of the instrument response indicates that the LOD has not changed. To monitor the instrument response, a quality control chart is constructed, as specified in section 8.4, except using calibration standard area counts rather than control standard concentrations. When the standard area counts are out-of-control, corrective action(s) must be taken before analysis may proceed. To make the ~~necessary~~ calculations, it is necessary to perform a multipoint calibration consisting of at least four "low" concentration levels, each above the LOD. The LOD must be calculated using the following equation [Ref. 9] ~~(Ref 9.2)~~:

$$\text{LOD} = \frac{|b| + (t \times s)}{m}$$

$$\text{LOD} = |A| + 3.3(S)$$

where each term in the equation is expressed in concentration units, and $|A|$ is the absolute value of the least squares X-intercept calculated from the multipoint data. $S|b|$ is the absolute value of the y-intercept, m is the slope of the linear regression, s is the standard deviation of at least five replicate determinations of the lowest concentration standard, and t is the t-factor for 99 percent confidence for a one-sided normal (Gaussian) distribution. The number of degrees of freedom is equal to the number of replicates, minus one. An abbreviated t-table is:

Degrees of Freedom	t-value
<u>4</u>	<u>3.7</u>
<u>5</u>	<u>3.4</u>
<u>6</u>	<u>3.1</u>
<u>7</u>	<u>3.0</u>

At least three replicates are required. The lowest standard must be of a concentration of at one to five times the estimated LOD detection limit. If data is not available in the concentration range near the detection limit, S may be estimated by:

$$S = RSD \times |A|$$

RSD is the relative standard deviation of the lowest standard analyzed.

8.7.1. The maximum allowable LOD for each compound is 20 ppbC propane. The calculated laboratory LOD must be equal to or lower than the maximum allowable LOD. All peaks identified as target compounds that are equal to or exceed the maximum allowable LOD must be reported. If the calculated laboratory LOD is less than the maximum allowable LOD, the laboratory may choose to set its reporting limit at either the maximum allowable LOD or the calculated laboratory LOD.

8.7.2. For the purposes of calculating the total mass (ppbC) of all species, the concentrations of all compounds below the LOD are considered to be zero.

8.8 Method No. 1002/Method No. 1003 Crossover Check For each sample, a compound shall be measured by both Method No. 1002 and Method No. 1003. The crossover compound shall be a compound that can reasonably be expected to be found and measured by both methods in the laboratory performing the analysis. The results obtained by the two methods should be compared and an acceptance criteria set for the relative percent difference.

9. ~~REFERENCES~~

9.1 ~~Standard Test Method for C₇ through C₆ Hydrocarbons in the Atmosphere by Gas Chromatography, American Standards for Testing Materials (ASTM) Standards on Chromatography (1981):~~

9.2 ~~U.S. Environmental Protection Agency, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (Method T03-15), EPA-600/4-84-041. Research Triangle Park, North Carolina, April 1989.~~

Part E

DETERMINATION OF C₆ TO C₁₂ HYDROCARBONS IN AUTOMOTIVE SOURCE SAMPLES BY GAS CHROMATOGRAPHY

METHOD NO. 1003

1. INTRODUCTION

- 1.1 This document describes a method of analyzing, by gas chromatography, C₆ to C₁₂ hydrocarbons (mid-range hydrocarbons) in the range of parts per billion carbon (ppbC) from automotive source samples. This method does not include sample collection procedures [Ref. 7] (~~Ref 9.1~~). The target hydrocarbons which shall be analyzed and reported by this method and Method 1002 are listed in attachment Appendix 1. All compounds on this list, when present in concentrations above the LOD, shall be measured and reported ("targeted") by either Method 1002 or Method 1003. Each laboratory should divide the list into light-end (Method 1002) and mid-range (Method 1003) hydrocarbons in the manner which best suits the laboratory instrumentation. All compounds on the list not targeted by Method 1003 must be targeted by Method 1002. ~~More compounds may be measured than those on the target list.~~
- 1.2 All definitions and abbreviations are contained in Appendix 2 of these test procedures.

2. METHOD SUMMARY

- 2.1 This is a ~~rapid~~ method intended for routine analysis.
- 2.2 The samples are received by the laboratory in Tedlar bags, which are sub-sampled into a ~~gas chromatograph (GC)~~ for separation and analysis analyses.
- 2.3 The gas chromatographic analysis is performed through a temperature-programmed capillary column. ~~operated using gradient temperature.~~ A ~~flame ionization detector (FID)~~ is used for detection. ~~A photoionization detector (PID) may be used to help with compound identification.~~
- 2.4 The sample is injected into the GC by means of gas sampling valves. Separation of the sample hydrocarbon mixture into its components ~~constituents~~ takes place in the chromatographic column. The chromatographic column and the corresponding operating parameters described in this method normally provide complete resolution of most target hydrocarbons.
- 2.5 The computerized GC data acquisition system identifies the hydrocarbons associated with each ~~of the peaks~~. The hydrocarbon concentrations are determined by integrating the peak areas and using a response calibration factor determined from ~~with~~ NIST-traceable standards.

3. INTERFERENCES AND LIMITATIONS

- 3.1 An ~~interference~~ interferent is any component present in the sample with a retention time similar to that of ~~any the~~ target hydrocarbons described in this method. To reduce interference error, proof of chemical identity may require ~~performance of~~ periodic confirmations using an alternate method and/or instrumentation, e.g., ~~gas chromatograph/mass spectrometer (GC/MS), photoionization detector (PID),~~ different column, etc.
- 3.2 The concentration of hydrocarbons in the range of interest is stable for at least 24 hours in the Tedlar sampling bags, provided the sample bags do not leak and are not exposed to bright light or excessive heat. Sampling bags must be shielded from direct sunlight to avoid losses from reaction of the reactive hydrocarbons. Samples must be analyzed within 24 hours.

4. INSTRUMENTATION AND APPARATUS

- 4.1 Tedlar bags, 2 mil in thickness, nominally 5 to 10 liters in capacity and equipped with quick-connect fittings, are used to contain the samples.
- 4.2 For manual sub-sampling into a GC, a ground glass syringe is used to transfer gaseous samples from Tedlar bags to the GC sample inlet. For automated systems, a sample loop is used to transfer gaseous samples from the Tedlar bag to the sample inlet of the GC. Sample aliquot size is chosen based on considerations of instrument sensitivity and/or linearity.
- 4.3 The GC is equipped with a FID, ~~a PID~~, and a gas sampling valve system.
- 4.4 A non-polar capillary column [e.g., J&W DB-1, 60 m x 0.32 mm ID, film thickness 1.0 ~~micron~~ μ] is used. Other columns may be used, provided the alternate(s) can be demonstrated to be equivalent or better with respect to precision, accuracy and resolution of all the target hydrocarbons.
- 4.5 A sample trap capable of being cryogenically cooled may be used.
- 4.5~~6~~ A computer-controlled data acquisition system is required for ~~the quantifying quantitation of~~ peak areas.

5. REAGENTS AND MATERIALS

- 5.1 Helium shall have a minimum purity of 99.995 percent. Higher purity helium may be required to achieve the LOD required by Section 8.7.1.
- 5.2 Hydrogen shall have a minimum purity of 99.995 percent.
- 5.3 Air shall be "Zero" grade. "Ultra-zero" grade may be required to achieve the LOD required by Section 8.7.1.
- 5.4 Nitrogen shall have a minimum purity of 99.998 percent.

5.5 Calibration Standard - The quantitative calibration standard for all target hydrocarbons shall be propane at a concentration level between 0.25 and 1 ppm-mole and within the calculated linearity of the method (see section 8.6). This propane standard must be traceable to a NIST-certified SRM ~~to a Standard Reference Material (SRM) certified for propane by the National Institute of Standards and Technology (NIST). NIST traceable means that the standard has been compared with not more than one intermediate standard, to a NIST-certified SRM.~~ A comparison between a SRM and a candidate standard will yield a secondary NIST traceable standard, while a comparison between a secondary NIST traceable standard and a candidate standard will yield a tertiary NIST traceable standard. A NIST SRM propane standard, a secondary NIST traceable propane standard, or a tertiary NIST traceable propane standard is required for calibration of Mmethod 1002 or 1003.

~~The minimum requirements for the manufacture and use of a secondary or tertiary NIST traceable propane standard shall be the following: 1) the standard must be packaged in aluminum cylinders which have been precleaned and passivated 2) a gas chromatograph shall be used to compare the candidate cylinders with the NIST traceable standard using either direct or interpolation comparison (In the direct comparison the analyte concentration for the candidate standard may not differ more than 10 percent from the analyte concentration of the NIST traceable standard; while in the interpolation comparison the analyte concentration of a candidate standard is bracketed between the analyte concentrations of the NIST SRM standards.); 3) analytes and balance gases in secondary candidate cylinders must be the same composition as the NIST SRM propane standards used in an interpolation comparison procedure, 4) hydrocarbon analytes (except propane) and balance gases may differ in secondary candidate cylinders from the NIST SRM propane standard used in a direct comparison procedure if there are no interferences with the propane measurement or stability, 5) comparison between a secondary and tertiary standard must be direct, and 6) all candidate cylinders must be analyzed a minimum of 4 times and stated uncertainties must be determined for all secondary and tertiary standard analytes, and 7) gas in the cylinder cannot be used when the pressure of the cylinder falls below 300 pounds per square inch.~~

~~It is recommended that either the laboratory or standard supplier(s) for the laboratory certify the secondary standards through the NIST Traceable Reference Material program or obtain Research Gas Material/Mixtures of propane standards from NIST for use as secondary standards.~~

5.6 Control Standard - A quality control standard, containing at least n- hexane, n-octane, n-decane, benzene, toluene, and m- or p-xylene with concentrations between 0.2 and 1 parts per million carbon (ppmC) based on a propane standard, is used for the following quality control purposes:

1. Daily update of control charts, and
2. Daily determination of marker retention time windows.

~~The control standard(s) must have concentrations verified against a NIST-traceable propane standard (See Section 5.5 for definition of NIST-traceable) when used for either LOD determinations or linearity checks. This verification can be performed at the laboratory conducting the sample analysis.~~

- 5.7 A high concentration standard (higher than the calibration standard), containing the target hydrocarbons listed in section 5.6 is used ~~semi-annually~~ for linearity determinations. The high ~~concentration calibration~~ standard must have concentrations verified against a NIST-traceable propane standard (See Section 5.5 for the definition of NIST-traceable). This verification can be performed at the laboratory performing the analysis.
- 5.8 Liquid nitrogen may be required ~~is used~~ to cool the cryogenic trap and column oven where applicable.

6. PROCEDURE

6.1 Typical operating conditions.

6.1.1 Suggested operating conditions for the manual GC are:

Helium carrier gas ~~average-linear~~ velocity: 30 cm/sec ~~centimeters/second~~ at 200°C
Nitrogen make-up gas flow: sufficient such that the total flow of helium plus nitrogen is 30 mL/min
Hydrogen gas flow (for FID): 30 mL/min
"Zero" air gas flow (for FID): 300 mL/min
Autozero FID ~~and PID~~ at: 0.0 min
Range 11, Attenuation 8 (or another suitable value)
Sample valve temperature: 150°C
Injector temperature: 150°C
Column Entrance Port temperature: 95°C
Detector temperature: 250°C
Column temperature: Initial temperature 0° C; 10°C/min to 200° C

6.1.2 Suggested operating conditions for the automated GC are:

Helium carrier gas ~~average-linear~~ velocity: 20 30 ~~cm/second~~ at 200° C
Nitrogen make-up gas flow: sufficient such that the total flow of helium plus nitrogen is 30 mL/min
Hydrogen gas flow (for FID): 30 mL/min
"Zero" air gas flow (for FID): 300 mL/min
~~Autozero FID and PID at 0.0 min~~
Range 11, attenuation 8 (or another suitable value)
Sample valve temperature: 150° C
Detector temperature: ~~250~~ 300 ° C
Column Temperature: Initial temperature ~~0~~ -50°C (5 min), 5° C/min to 50°C, 10°C/min to 200°C

6.2 Data Reduction

6.2.1 All peaks identified as target compounds (Appendix 1) at or above the ~~maximum allowable limit of detection (LOD)~~ are reported (Section 8.7). ~~At the laboratory's discretion, peaks at or above the LOD calculated in section 8.7 may be reported. The calculated LOD must be lower than the maximum allowable LOD.~~

6.2.2 The results are calculated from the FID responses. ~~The PID responses are used to help with peak identifications as the PID responds more strongly to aromatics and olefins.~~

6.2.3 The results are examined to see that the peaks are correctly identified and integrated.

6.2.4 After running a particularly "dirty" sample, the analyst should run a blank before proceeding to the next sample as there may be sample carryover, or flush the sampling system with air.

6.2.5 The peak identifications provided by the computer are reviewed and, if necessary, corrected using the following procedure and criteria:

- (1) The relative retention indices from GC/MS analyses are used to help confirm peak identifications.
- (2) The primary peak identification is done by the computer using the relative retention times based on reference calibration runs.
- (3) Confirm that the relative peak heights ~~largest peaks~~ of the sample run ("fingerprint") match the typical fingerprint seen in past sample runs.
- (4) Compare the relative retention time of the sample peaks with those of reference runs.
- (5) Any peak with a reasonable doubt is labeled 'Unidentified'.

6.2.6 The concentrations of the hydrocarbons are calculated by an electronic integrator device.

6.2.7 Target compounds which coelute are reported as the major component, as determined by the analysis of several samples by GC/MS or other methods. An exception to this is m- and p-xylene, where GC/MS data and fuel profiles are used to determine the relative contribution of each component to the peak. This method was used to determine the m- and p-xylene MIR value given in Appendix 1.

7. CALCULATIONS

- 7.1 The target hydrocarbon concentrations, in ppbC, are calculated by the data system using propane as an external standard.

$$\text{Concentration}_{\text{sample}} \text{ (ppbC)} = \text{Peak Area}_{\text{sample}} \times \text{Response Factor}$$

where the response Factor (RF) is calculated during daily calibration by:

$$\text{RF} = \frac{\text{Concentration of NIST-traceable propane standard, ppbC}}{\text{Area of propane peak}}$$

8. QUALITY CONTROL

- 8.1 Blank Run. A blank (pure nitrogen or helium) is run once daily before running the calibration standard, control standard, and samples. All target hydrocarbon concentrations from the blank analysis must be below the LOD before the analysis may proceed. As an alternative to a daily blank run, a daily partial blank check in tandem with a weekly blank run may be used. A partial blank check is where the calibration standard, consisting of only propane and make-up gas (all organic compounds except methane and propane are below 2 percent of the propane standard concentration), is run daily and is checked for contamination except in the propane region of the chromatograph. The weekly blank run will provide a check on contamination in the propane region of the chromatograph.

- 8.2 Calibration Run. One run of the calibration standard is performed per day to generate the response calibration factor needed for ~~quantitating~~ quantifying sample analyses.
- 8.3 Control Standard Run. One run of the quality control standard is performed daily. Measurements of all compounds in the control standard must fall within the control limits before sample analysis may proceed. To meet this requirement, it may be necessary to inspect and repair the GC, and rerun the calibration and/or control standards.
- 8.4 Control Charts. ~~A Quality control chart(s) is are~~ maintained for each component of the control ~~standard sample~~. The control charts, used on a daily basis, establishes that the method is "in-
"statistical control". The following describes how to construct a typical control chart:
1. Obtain at least 20 daily control ~~standard sample~~ results,
 2. Calculate the ~~average~~ control ~~standard sample mean~~ concentration and standard deviation(s) for the each target hydrocarbon, and
 3. Create a control chart for the each target hydrocarbon by placing the concentration on the Y-axis and the date on the X-axis. ~~Establish~~ Draw an upper warning limit and a lower warning limit at two standard deviations (2s) above and below the average concentration. ~~Establish~~ Draw an upper control limit and a lower control limit at three standard deviations (3s) above and below the average concentration.

~~The control sample must be "in-control" for~~ The measured concentrations of all target hydrocarbons contained in the control standard sample must be within the control limits ("in-control") for the sample results to be considered acceptable. A control ~~standard sample~~ measurement is considered to be "out-of-control" when the analyzed value ~~of the sample measurement~~ exceeds the 3s limit, or two successive control ~~standard sample~~ measurements of the same analyte exceed the 2s limit.

- 8.5 Duplicates. A duplicate analysis of one sample is performed at least once a day. The relative percent difference (RPD) is calculated for each duplicate run:

$$\text{RPD (\%)} = \frac{\text{Difference between duplicate and original measurements} \times 100}{\text{Average of duplicate original measurements}}$$

For each compound in the control standard, the allowable RPD depends on the average concentration level for the duplicate runs, as shown in the following table:

<u>Average Measurement for Duplicate Runs</u>			<u>Allowable RPD (%)</u>
1 to 10	times	LOD	100
10 to 20	"	"	30
20 to 50	"	"	20
Greater than 50	"	"	15

If the results of the duplicate analyses do not meet these criteria for all compounds in the control standard, the sample must be reanalyzed. If the criteria are still not met, all sample results for the day from this instrument must be deleted and the samples reanalyzed.

- 8.6 Linearity. A multipoint calibration to ~~confirm check for~~ instrument linearity is performed for all target hydrocarbons in the control standard ~~for new instruments, after making instrument modifications which can affect linearity, and~~ at least once every ~~year six months~~; ~~unless a daily check of the instrument response indicates that the linearity has not changed.~~ To monitor the instrument response, a quality control chart is constructed, as specified in section 8.4, ~~except using calibration standard area counts rather than control standard concentrations.~~ When the standard area counts are out-of-control, corrective action(s) must be taken before analysis may proceed. The multipoint calibration consists of at least five concentration or mass loading levels (using smaller or larger volume sample sizes of existing standards is acceptable), ~~each~~ above the LOD, ~~evenly~~ distributed over the range of expected sample concentration linearity of the instrument. Each concentration level is measured at least twice. A linear regression analysis is performed using concentration and average area counts to determine the regression correlation coefficient (r). The r must be greater than 0.995 to be considered sufficiently linear for one point calibrations.
- 8.7 Limit of Detection. The LOD ~~limit of detection~~ for the target hydrocarbons in the control standard must be determined ~~for new instruments and after making instrument modifications which can affect linearity and/or sensitivity and~~ at least once every ~~year six months~~; ~~unless a daily check of the instrument response indicates that the LOD has not changed.~~ To monitor the instrument response, a quality control chart is constructed, as specified in section 8.4, ~~except using calibration standard area counts rather than control standard concentrations.~~ When the standard area counts are out-of-control, corrective action(s) must be taken before analysis may proceed. To make the ~~necessary~~ calculations, it is necessary to perform a multipoint calibration consisting of at least four "low" concentration levels, ~~each~~ above the LOD. The LOD must be calculated using the following equation [Ref. 7] (~~Ref 9.1~~):

$$\text{LOD} = \frac{|b| + (t \times s)}{m}$$

$$\text{LOD} = |A| + 3.3(S)$$

where ~~each term in the equation is expressed in concentration units, and~~ ~~|A|~~ is the absolute value of the least squares ~~X-intercept calculated from the multipoint data.~~ ~~S~~ ~~|b|~~ is the absolute value of the y-intercept, ~~m~~ is the slope of the linear regression, ~~s~~ is the standard deviation of at least five replicate determinations of the lowest concentration standard, and ~~t~~ is the t-factor for 99 percent confidence for a one-sided normal (Gaussian) distribution. The number of degrees of freedom is equal to the number of replicates, minus one. An abbreviated t-table is:

<u>Degrees of Freedom</u>	<u>t-value</u>
<u>4</u>	<u>3.7</u>
<u>5</u>	<u>3.4</u>
<u>6</u>	<u>3.1</u>
<u>7</u>	<u>3.0</u>

~~At least three replicates are required. The lowest standard must be of a concentration of at one to five times the estimated LOD detection limit. If data is not available in the concentration range near the detection limit, S may be estimated by:~~

$$\underline{S} = \text{RSD} \times \underline{A}$$

~~RSD is the relative standard deviation of the lowest standard analyzed.~~

8.7.1 The maximum allowable LOD for each any compound is 20 ppbC propane. The calculated laboratory LOD must be equal to or lower than the maximum allowable LOD. All peaks identified as target compounds that are equal to or exceed the maximum LOD must be reported. If the calculated laboratory LOD is less than the maximum allowable LOD, the laboratory may choose to set its reporting limit at either the maximum allowable LOD or the calculated laboratory LOD.

8.7.2 For the purposes of calculating the total mass (ppbC) of all species, the concentrations of the compounds below the LOD are considered to be zero.

- 8.8 Method No. 1002/Method No. 1003 Crossover Check. For each sample a compound shall be measured by both Method No. 1002 and Method No. 1003. The crossover compound shall be a compound that can reasonably be expected to be found and measured by both methods in the laboratory performing the analysis. The results of the two analyses should be compared and an acceptance criteria set for the relative percent difference.

~~9. REFERENCE~~

- 9.1 ~~U.S. Environmental Protection Agency, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (Method T93-15), EPA-600/4-89-017, Research Triangle Park, North Carolina, June 1989~~

Part F
DETERMINATION
OF ALDEHYDE AND KETONE COMPOUNDS
IN AUTOMOTIVE SOURCE SAMPLES
BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

METHOD NO. 1004

1. INTRODUCTION

- 1.1 This document describes a method of analyzing automotive engine exhaust for aldehyde and ketone compounds (carbonyls) using impingers, containing acidified 2,4-dinitrophenylhydrazine (DNPH)-absorbing solution, or DNPH-impregnated cartridges. Carbonyl masses ranging between 0.02 to 200 µg are measured by this method. The "target" carbonyls which shall be analyzed and reported by this method are listed in Appendix 1. ~~are formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, butyraldehyde, hexanal, benzaldehyde, methyl-ethyl-ketone, methacrolein, crotonaldehyde, valeraldehyde, and m- or p-tolualdehyde~~ All of these carbonyl compounds, when present in concentrations above the LOD, shall be reported.
- 1.2 This procedure is derived from a method used by Hull [Ref. 10] (~~Ref. 9-1~~).
- 1.3 All definitions and abbreviations are contained in Appendix 2 of these test procedures.

2. METHOD SUMMARY

- 2.1 The samples are received by the laboratory in sample collection cartridges or impingers (See Section 4.2). The absorbing solution (2,4-DNPH) complexes the carbonyl compounds into their diphenylhydrazone derivatives. The cartridges are then eluted with 5 mL acetonitrile.
- 2.2 Separation and analysis are is performed using a ~~High-Performance-Liquid-Chromatograph~~ HPLC with an ultraviolet detector.

3. INTERFERENCES AND LIMITATIONS

- 3.1 An ~~interferent~~ interference is any detectable compound present in the sample with a retention time very similar to that of any the target carbonyls described in this method. To reduce interference error, proof of chemical identity may require ~~performance of~~ periodic confirmations using an alternate method and/or instrumentation, e.g., alternative HPLC columns or mobile phase compositions.

- 3.2 If samples are not analyzed the same day as received, they must be ~~transferred to glass bottles, sealed, and~~ refrigerated at a temperature below 40°F. Impinger solutions must first be transferred to glass bottles and sealed. Refrigerated samples are stable for up to 30 days.
- 3.3 When using the DuPont Zorbax column described in Section 4.1.5, methyl ethyl ketone (MEK) and butyraldehyde tend to coelute.
- 3.4 When using the Delta Bond column described in Section 4.1.5, formaldehyde tends to coelute with an unknown, non-carbonyl compound, and the tolualdehyde isomers tend to coelute. The guard column for the Delta Bond column must also be changed frequently in order to prevent the coelution of butyraldehyde and methacrolein.

4. **INSTRUMENT AND APPARATUS**

- 4.1 The HPLC analytical system consists of the following:
- 4.1.1 Dual high pressure pumps.
 - 4.1.2 Automated gradient controller or pump module controller.
 - 4.1.3 Temperature controller module for the column oven.
 - 4.1.4 A liquid autosampler.
 - 4.1.5 The primary system incorporates two DuPont Zorbax ODS columns in tandem and a guard column, (2 ~~centimeters~~ (cm) long packed with LC18 5 ~~micrometers~~ (µm) pellicular beads). The secondary system incorporates a Delta Bond AK (4.6 mm ID x 200 mm) packed column with a guard column 2 cm long packed with LC18 5 µm pellicular beads or equivalent). Other columns may used, provided the alternate(s) can be demonstrated to be equivalent or better with respect to precision, accuracy and resolution of all target carbonyls.
 - 4.1.6 An ultraviolet/visible (UV/VIS) detector.
 - 4.1.7 Data system for peak integration.
- 4.2 Sample collection containers are glass impingers; or DNPH-impregnated cartridges may also be used.

5. **REAGENTS AND MATERIALS**

- 5.1 Acetonitrile, HPLC grade, (Burdick and Jackson or equivalent).
- 5.2 Water, HPLC grade, (Burdick and Jackson or equivalent).

- 5.3 ~~2,4-Dinitrophenylhydrazine (DNPH), purified, Radian Corporation Eastman or equivalent. Unpurified DNPH must be~~ ; recrystallized twice from acetonitrile. The recrystallized DNPH is checked for contaminants by injecting a dilute solution of DNPH in contaminant-free acetonitrile into the HPLC.
- 5.4 Sulfuric acid, or perchloric acid, analytical reagent grade, (Baker Analyzed or equivalent).
- 5.5 ~~Synthesized 2,4-dinitrophenylhydrazones (ref. 9.2) The carbonyl/2,4-dinitrophenylhydrazone (DNPH) complexes [Ref. 11] listed in Table F-1 may be purchased (e.g., Radian Corporation, in 1.2 mL ampules) or prepared in the laboratory. In-house standards must be recrystallized at least three times from 95 percent ethanol. are:~~

TABLE F-1
PROPERTIES OF CARBONYL/2,4-DNPH COMPLEXES

<u>Complex</u>	<u>Molecular Weight (g/mole)</u>	<u>Melting Point °C</u>
<u>formaldehyde</u>	<u>210.15</u>	<u>165-166</u>
<u>acetaldehyde</u>	<u>224.18</u>	<u>152-153</u>
<u>acrolein</u>	<u>236.19</u>	<u>165¹</u>
<u>acetone</u>	<u>238.20</u>	<u>125-127</u>
<u>propionaldehyde</u>	<u>238.20</u>	<u>144-145</u>
<u>butyraldehyde</u>	<u>252.23</u>	<u>119-120</u>
<u>hexanaldehyde</u>	<u>280.28</u>	<u>106-107</u>
<u>benzaldehyde</u>	<u>286.25</u>	<u>240-242</u>
<u>methyl-ethyl-ketone</u>	<u>252.53</u>	<u>117-118</u>
<u>methacrolein</u>	<u>250.21</u>	<u>200-201</u>
<u>crotonaldehyde</u>	<u>250.21</u>	<u>185-188</u>
<u>valeraldehyde</u>	<u>266.26</u>	<u>107-108</u>
<u>m- tolualdehyde</u>	<u>300.27</u>	<u>212</u>

~~5.5.1 Formaldehyde/2,4-dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 168°C.~~

~~5.5.2 Acetaldehyde/2,4-dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 166-168°C.~~

~~5.5.3 Acrolein/2,4-dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol and acetonitrile, melting point (m.p.) 158-159°C.~~

~~5.5.4 Acetone/2,4-dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol; melting point (m.p.) 126-128°C.~~

~~5.5.5 Propionaldehyde/2,4-dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 138-140°C.~~

¹ This compound has been known to decompose.

5.5.6 ~~Butyraldehyde/2,4-dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 109-111°C.~~

5.5.7 ~~Hexanal/2,4-dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 105-106°C.~~

5.5.8 ~~Benzaldehyde/2,4-dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 235-237°C.~~

5.5.9 ~~Methyl-ethyl-ketone/2,4-dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 115-116°C.~~

5.5.10 ~~Methacrolein/2,4-dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 206°C.~~

5.5.11 ~~Crotonaldehyde/2,4-dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 185-188°C.~~

5.5.12 ~~Valeraldehyde/2,4-dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 103-106°C.~~

5.5.13 ~~m- or p-Tolualdehyde/2,4-dinitrophenylhydrazone, recrystallized three times from 95 percent ethanol, melting point (m.p.) 239°C.~~

- 5.6 Stock Calibration Standard - A stock calibration standard is prepared by diluting the target carbonyl/2,4-DNPH complexes with acetonitrile, e.g., a typical 100-ml acetonitrile standard stock calibration standard solution contains : approximately 5 to 15 mg/mL of each target carbonyl/DNPH complex.

~~14.8 milligrams (mg) formaldehyde/2,4-dinitrophenylhydrazone—
 8.4 mg acetaldehyde/2,4-dinitrophenylhydrazone—
 6.0 mg acrolein/2,4-dinitrophenylhydrazone—
 5.7 mg acetone/2,4-dinitrophenylhydrazone—
 4.7 mg propionaldehyde/2,4-dinitrophenylhydrazone—
 5.0 mg butyraldehyde/2,4-dinitrophenylhydrazone—
 5.0 mg benzaldehyde/2,4-dinitrophenylhydrazone—
 5.0 mg hexanal/2,4-dinitrophenylhydrazone—
 5.0 mg methyl-ethyl-ketone/2,4-dinitrophenylhydrazone—
 5.0 mg methacrolein/2,4-dinitrophenylhydrazone—
 5.0 mg crotonaldehyde/2,4-dinitrophenylhydrazone—
 5.0 mg valeraldehyde/2,4-dinitrophenylhydrazone—
 5.0 mg m or p-tolualdehyde/2,4-dinitrophenylhydrazone—
 Commercial standards are also available for these compounds.~~

- 5.7 Working Standard - A working standard is prepared when required by diluting the stock calibration solution, making sure that the highest concentration of the standard is above the expected test level; e.g., ± 5 mL of the stock calibration solution is diluted to 100 20 mL.
- 5.8 Control Standard - A quality control standard, containing all target carbonyls/2,4-DNPHdinitrophenylhydrazone complexes within the typical concentration range of real samples, is analyzed to monitor the precision of the analysis of each target carbonyl. update daily control charts. The control standard may be prepared by batch mixing old samples and

stirring for 24 hours. All target compounds except acrolein have been found to be stable in the control standard. Commercial standards are also available for these compounds.

6. PROCEDURE

- 6.1.1 ~~For systems collecting the samples via impingers, a~~ An absorbing solution is prepared by dissolving 0.11 - 0.13 grams of recrystallized DNPH in 1 ~~liter (L)~~ of HPLC grade acetonitrile. The absorbing solution should be prepared at least every two weeks. Each batch of acetonitrile used in this procedure is checked for oxygenated impurities by adding it to a ~~addition of~~ contaminant-free dilute solution of DNPH and analyzing by ~~ed in the~~ HPLC. ~~Cartridges should be sealed and refrigerated at less than 40°F.~~

6.1.12. In the laboratory, pipette 15 mL of the DNPH absorbing solution into each of the 30 mL ~~midjet~~ impingers for each emission test. Add 0.1 mL of 2.85 N sulfuric acid or 0.15 mL of 3.8M perchloric acid to each impinger.

~~6.1.3 DNPH impregnated cartridges may also be used to collect carbonyl samples. At the volumes being sampled (1 L/minute), no back-up cartridge is needed. Leave the cartridges capped.~~

- 6.2 For systems collecting the samples via cartridges, DNPH-impregnated cartridges shall be sealed and refrigerated, at a temperature less than 40°F, upon receipt from manufacturer, until ready for use.

6.2.1 At the exhaust volumes being sampled (1 L/min), a back-up cartridge may be required for CVS phase 1 but no back-up cartridge is needed for CVS phases 2 and 3.

- ~~6.2 Connect the impinger pairs in series and cap the open ends to prevent contamination. (These sets of impingers (cartridges) are picked up by the automotive test personnel for sampling.)~~

- 6.3 ~~After the sampling has been completed, cap the impingers or cartridges and return them to the laboratory. After sampling~~ At the laboratory, uncap and place all the impingers and the field blank impinger in preheated water at 70-80°C for 30 minutes (min) to complete derivatization. Heating is not required when using perchloric acid.

6.3.1 ~~For sampling with~~ cartridges, remove the caps and extract with 5 mL acetonitrile, running the extract into glass storage bottles.

- 6.4 Remove the impingers from the water bath and cool to room temperature. Replace any lost solvent by adding acetonitrile to the 15 mL mark.

6.4.1 Replacing lost solvent is not required when using an internal standard method (Section 7.4).

- 6.5 Transfer the solution from each impinger/cartridge to glass vials and seal with new septum screw caps.

- 6.6 Place the vials containing blank, working standard, control standard, and samples into the autosampler for subsequent injection into an HPLC. Suggested standard operating conditions for the HPLC are: configured as follows:

Primary System:

Columns: 4.6 ~~millimeters~~ (mm) ID x 250 mm x 1/4 inches OD Dupont Zorbax ODS two columns in series, Guard column - 2 cm long packed with C18 5 µm pellicular

Column temperature: 40°C

Detector: UV/VIS at 360 ~~nanometers~~ nm

Sample volume: ~~20~~ 10 microliters µL

Solvent A: acetonitrile

Solvent B: 10 percent (volume/volume) methanol in water

Flow: 1 mL/min

Program - 50 percent A, 50 percent B 0 (initial time)
65 percent A, 35 percent B 0 to 5 2 min
100 percent A, 0 percent B 5 2 to 35 22 min
50 percent A, 50 percent B 35 22 to 36 37 min
~~50 percent A, 50 percent B 36 to 46 " (hold)~~

Under the above configuration, methyl ethyl ketone and butyraldehyde tend to coelute. In order to report these compounds, it is necessary to analyze the samples using a secondary system. The tolualdehyde isomers (m-, p-, and o-) are separated using this configuration. The reporting of tolualdehyde is addressed in Section 7.4.

Secondary System:

Columns: Delta Bond AK C18 (4.6 mm ID x 200 mm x 1/4 in OD) packed column,
Guard column - 2 cm long packed with C18 5 µm pellicular

Column temperature: 40° C

Detector: UV/VIS at 360 nm

Sample volume: 10 µL

Solvent A: purified water

Solvent B: acetonitrile

Flow: 1.5 mL/min

Program - 65 percent A, 35 percent B (initial time)
65 percent A, 35 percent B 0 - 5.5 min
50 percent A, 50 percent B 5.5 - 8.0 min
35 percent A, 65 percent B 8.0 - 11.1 min
65 percent A, 35 percent B 11.0 - 13.0 min

This secondary system is not used to report all compounds because formaldehyde tends to coelute with a non-carbonyl compound. If this coelution is resolved, the secondary system may be used alone to analyze all carbonyl compounds. The tolualdehyde isomers, however, are not separated with this configuration. The reporting of tolualdehyde is addressed in Section 7.4.

Data System: The outputs from the UV/VIS detector are sent to a PC-controlled data acquisition system.

- 6.7 The peak integrations are corrected as necessary in the data system. Any misplaced baseline segments are corrected in the reconstructed chromatogram.
- 6.8 The target carbonyl peaks at or above the ~~maximum allowable limit of detection~~ LOD are reported (Section 8.10). ~~At the laboratory's discretion, peaks at or above the LOD calculated in section 8.10 may be reported. The calculated LOD must be lower than the maximum allowable LOD.~~

7. CALCULATIONS

- 7.1 For each target carbonyl, the carbonyl mass is calculated from its carbonyl/2,4-dinitrophenylhydrazone DNPH mass.
- 7.2 The mass of each carbonyl compound, ~~µg~~ per ~~15-mL~~ impinger or cartridge, is determined by the following calculation:

$$\text{Mass}_{\text{sample}} = \text{Peak Area}_{\text{sample}} \times \text{Response Factor} \times \text{Impinger (or Cartridge) volume(mL)} \times B$$

where B is the ratio of the molecular weight of the carbonyl compound to its 2,4-dinitrophenylhydrazone derivative and where the response factor (RF) for each carbonyl is calculated during the calibration by:

$$\text{RF} = \frac{\text{Concentration}_{\text{standard}} (\text{units } \mu\text{g 2,4-DNPH species/mL})}{\text{Peak Area}_{\text{standard}}}$$

- 7.3 For tolualdehyde, the sum of all isomers present is reported as m-tolualdehyde.
- 7.3.1 Under the conditions of the primary system in Section 6.6, the isomers are separated. The m-tolualdehyde response factor is applied to each peak and the sum reported as m-tolualdehyde.
- 7.3.2 Under the conditions of the secondary system in Section 6.6, the isomers coelute. The m-tolualdehyde response factor is applied to the single tolualdehyde peak. This concentration is reported as m-tolualdehyde.
- 7.4 An internal standard method may also be used.
- ## 8. QUALITY CONTROL
- 8.1 Reagent Blanks. The solvents used are of the highest HPLC grade and are ~~checked at least daily for impurities by conducting blank analyses.~~ tested for impurities when a new lot number is used. If this lot number is found to be acceptable, (no carbonyls present at concentrations at or above the LOD), daily blank analysis is not performed.

8.2 Carbonyl/2,4-DNPH Phenylhydrazone Purity. The carbonyl/ 2,4-dinitrophenylhydrazones DNPHs are checked for purity by their melting points and their chromatograms (See Table F-1). Analysis of the solution of carbonyl/2,4-DNPH phenylhydrazone must yield only the peak of interest. No contaminant peaks above the LOD should be observed.

8.3 Calibration Run. One run of the calibration standard is performed ~~at least~~ daily to generate the response ~~calibration~~ factors needed for quantifying sample analyses.

8.4 Control Standard Run. One run of the quality control standard is performed ~~at least~~ daily after the calibration run. Measurements of all compounds in the control standard, except acrolein, must fall within the control limits before sample analysis may proceed. To meet this requirement, it may be necessary to rerun the calibration and control standards, and inspect and repair the HPLC.

8.5 Control Charts. ~~A~~ Quality control chart(s) ~~is are~~ maintained for each component of the control sample, except acrolein. The control charts, used on a daily basis, ~~establishes~~ that the method is "in- statistical control." The following describes how to construct a typical control chart:

1. Obtain at least 20 daily control standard sample results,
2. Calculate the ~~average~~ control standard sample mean concentration and standard deviation(s) for the each target analyte, and
3. Create a control chart for the each target analyte by placing the concentration on the Y-axis and the date on the X-axis. Establish ~~Draw~~ an upper warning limit and a lower warning limit at two standard deviations (2s) above and below the average concentration. Establish ~~Draw~~ an upper control limit and a lower control limit at three standard deviations (3s) above and below the average concentration.

~~The control sample must be "in-control" for~~ The measured concentrations of all target analytes contained in the control standard must be within the control limits ("in-control") for the sample results to be considered acceptable. ~~Due to the low variability of the carbonyl control standard measurements, a~~ A control standard sample measurement is considered to be "out-of-control" when the analyzed value exceeds either the 3s limit, or the range of $\pm 10\%$ of the mean control measurement, whichever is greater, or if two successive control standard sample measurements of the same analyte exceed the 2s limit. No control requirements have been established for acrolein, since it has been shown to degrade over time.

8.6 Field Blanks. One field blank is analyzed for each set of impingers for each emission test. One cartridge for each ~~per~~ batch number used is analyzed as a field blank.

8.7 At least ~~One~~ cartridge per batch is analyzed as a batch blank.

8.8 Duplicates. A duplicate analysis of one sample is performed at least once a day. The relative percent difference (RPD) is calculated for each duplicate run:

$$\text{RPD(\%)} = \frac{\text{Difference between duplicate and original measurements}}{\text{Average of duplicate and original measurements}} \times 100$$

For each compound, the allowable RPD depends on the average concentration level for the duplicate runs, as shown in the following table:

<u>Average Measurement for Duplicate Runs</u>		<u>Allowable RPD (%)</u>
1 to 10	times LOD	100
10 to 20	" "	30
20 to 50	" "	20
Greater than 50	" "	15

If the results of the duplicate analyses do not meet these criteria for all target carbonyls, the sample must be reanalyzed. If the criteria are still not met, all sample results analyzed during the day from this instrument must be deleted and the samples reanalyzed.

8.9 Linearity. A multipoint calibration to ~~confirm~~ check for instrument linearity is performed for all target analytes for new instruments, after making instrument modifications which can affect linearity, and at least once every year. ~~six months~~. The multipoint calibration consists of at least five concentration or mass loading levels (using smaller or larger volume sample sizes of existing standards is acceptable), each above the LOD, ~~evenly~~ distributed over the range of expected sample concentration ~~linearity of the instrument~~. Each concentration level is measured at least twice. A linear regression analysis is performed using concentration and average area counts to determine regression correlation coefficient (r). The r must be greater than 0.995 to be considered linear for one point calibrations.

8.10 Limit of Detection. The ~~limit of detection~~ LOD for the target analytes must be determined for new instruments, after making instrument modifications which can affect the LOD and at least once per year. ~~every six months~~. To make the ~~necessary~~ calculations, it is necessary to perform a multipoint calibration consisting of at least four "low" concentration levels, each above the LOD. The LOD must be calculated using the following equation [Ref. 7] (~~Ref. 9.3~~):

$$\text{LOD} = \frac{|b| + (t \times s)}{m}$$

$$\text{LOD} = |A| + 3.3(S)$$

where ~~each term in the equation is expressed in concentration units, and~~ |A| is the absolute value of the least squares X-intercept calculated from the multipoint data. S |b| is the absolute value of the y-intercept, m is the slope of the linear regression, s is the standard deviation of at least five replicate determinations of the lowest concentration standard, and t is the t-factor for 99 percent confidence for a one-sided normal (Gaussian) distribution. The number of degrees of freedom is equal to the number of replicates, minus one. An abbreviated t-table is:

<u>Degrees of Freedom</u>	<u>t-value</u>
<u>4</u>	<u>3.7</u>
<u>5</u>	<u>3.4</u>
<u>6</u>	<u>3.1</u>

At least three replicates are required. The lowest standard must be of a concentration of at one to five times the estimated LOD detection limit. If data is not available in the concentration range near the detection limit, S may be estimated by:

$$\underline{S} = \text{RSD} \times \sqrt{A}$$

RSD is the relative standard deviation of the lowest standard analyzed.

An example of typical LODs is given in the table below:

<u>Compound</u>	<u>LOD (ug/ml)</u>
Formaldehyde/2,4-dinitrophenylhydrazine	0.048
Acetaldehyde/2,4-dinitrophenylhydrazine	0.011
Acrolein/2,4-dinitrophenylhydrazine	0.006
Acetone/2,4-dinitrophenylhydrazine	0.004
Propionaldehyde/2,4-dinitrophenylhydrazine	0.016
Butyraldehyde/2,4-dinitrophenylhydrazine	0.06*
Hexanal/2,4-dinitrophenylhydrazine	0.019
Benzaldehyde/2,4-dinitrophenylhydrazine	0.027
Methyl-ethyl-ketone/2,4-dinitrophenylhydrazine	-*
Methacrolein/2,4-dinitrophenylhydrazine	-
Crotonaldehyde/2,4-dinitrophenylhydrazine	0.016
Valeraldehyde/2,4-dinitrophenylhydrazine	0.009
m-or p-Tolualdehyde/2,4-dinitrophenylhydrazine	-

<u>CAS Nos.</u>	<u>Compound</u>	<u>LOD (ug/ml)</u>
00050-00-0	Formaldehyde	0.007
00075-07-0	Acetaldehyde	0.002
00107-02-8	Acrolein	0.002
00067-64-1	Acetone	0.001
00123-38-6	Propionaldehyde	0.004
00123-72-8	Butyraldehyde*	0.019
00066-25-1	Hexanal	0.007
00100-52-7	Benzaldehyde	0.010 0.004
00078-93-3	Methyl Ethyl Ketone*	-
00078-85-3	Methacrolein	-
04170-30-3	Crotonaldehyde	0.016
00110-62-3	Valeraldehyde	0.009
00104-87-0	p-Tolualdehyde	-** or
00620-23-5	m-Tolualdehyde	-**

* Butyraldehyde may co-elute with methyl-ethyl-ketone

**p-Tolualdehyde may co-elute with m-Tolualdehyde and o-Tolualdehyde

8.10.1 The maximum allowable LOD is 0.06 µg carbonyl derivative/mL. The calculated laboratory LOD must be equal to or lower than the maximum allowable LOD. All peaks identified as target compounds that are equal to or exceed the maximum allowable LOD must be reported. If the calculated laboratory LOD is less than the maximum allowable LOD, the laboratory may choose to set its reporting limit at either the maximum allowable LOD or the calculated laboratory LOD.

8.10.2 For the purpose of calculating the total mass of all species, the concentration of the compounds below the LOD are considered to be zero.

~~9. REFERENCES~~

~~9.1 Hull, L.A., Procedures for 2,4-Dinitrophenylhydrazone Aldehyde-Ketone Air Analysis, Internal Report at U.S. EPA.~~

~~9.2 Shriner, R.L. and Fuson, R.C., Identification of Organic Compounds, 2nd. Ed., John Wiley and Sons, Inc., 1940, p. 143.~~

~~9.3 U.S. Environmental Protection Agency, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (Method T03-15), EPA-600/4-89-017, Research Triangle Park, North Carolina, June 1989.~~

Part G

DETERMINATION OF NMOG MASS EMISSIONS

1. INTRODUCTION

- 1.1 ~~Non-methane organic gases (NMOG)~~ mass emissions consist of non-methane hydrocarbons and oxygenated hydrocarbons.
- 1.2 All definitions and abbreviations are set forth in Appendix 2 of these test procedures.

2. NMOG WEIGHTED MASS EMISSIONS

- 2.1 NMOG weighted mass (wm) emissions shall be calculated as follows:

$$\text{NMOG}_{\text{wm}} = \Sigma \text{NMHC}_{\text{wm}} + \Sigma \text{ROH}_{\text{wm}} + \Sigma \text{RHO}_{\text{wm}}$$

Non-methane hydrocarbon weighted mass emissions (NMHC_{wm}) can be determined by either ~~flame ionization detection (FID)~~ or ~~gas chromatography (GC)~~. If the FID method is used to calculate NMHC_{wm} , refer to Part B of these test procedures entitled, "Determination of Non-Methane Hydrocarbon Mass Emissions by Flame Ionization Detection." If the GC method is used to calculate NMHC_{wm} , refer to ~~the section 3, "Speciated Hydrocarbon Mass Emissions Calculation"~~ section 3, "Speciated Hydrocarbon Mass Emissions Calculation" contained herein. Carbonyl weighted mass emissions (RHO_{wm}) are to be calculated according to ~~the section 5 "Carbonyl Mass Emissions Calculation"~~ section 5 "Carbonyl Mass Emissions Calculation" contained herein. For alcohol fueled vehicles, alcohol weighted mass emissions (ROH_{wm}) are to be calculated according to ~~the section 4 "Alcohol Mass Emissions Calculation"~~ section 4 "Alcohol Mass Emissions Calculation" contained herein.

3. SPECIATED HYDROCARBON MASS EMISSIONS CALCULATION

1. INTRODUCTION

- 1.1 Vehicular exhaust emissions are measured according to the ~~Federal Test Procedure~~ FTP [Ref. 1] (†). For each of the three phases of the FTP, a tedlar bag of 0.5 ft³ capacity is used to collect a dilute exhaust sample. A fourth 0.5 ft³ tedlar bag is used to collect a composite dilution air (background) sample from all three phases of the FTP. All bag samples are analyzed according to Method No. 1002 (Part D of these test procedures) and Method No. 1003 (Part E of these test procedures) to determine the dilute exhaust and dilution air concentrations of individual hydrocarbon compounds. The measured hydrocarbon compound concentrations are used in the following equations to calculate the weighted mass emissions of each hydrocarbon compound.

2. HC MASS EMISSIONS CALCULATION PER TEST PHASE

$$2.1 \quad HC_{\text{mass } n} = (HC_{\text{conc}} * HC_{\text{dens}} * VMIX * 10^{-6}) / (\text{Carbon No.})$$

$$2.2 \quad HC_{\text{conc}} = HC_e - (HC_d * (1 - (1 / DF)))$$

NOTE: If HC_{conc} is calculated to be less than zero, then $HC_{\text{conc}} = 0$.

3. WEIGHTED HC MASS EMISSIONS CALCULATION

$$3.1 \quad HC_{\text{wm}} = 0.43 * \frac{(HC_{\text{mass } 1} + HC_{\text{mass } 2})}{(D_{\text{phase } 1} + D_{\text{phase } 2})} + 0.57 * \frac{(HC_{\text{mass } 3} + HC_{\text{mass } 2})}{(D_{\text{phase } 3} + D_{\text{phase } 2})}$$

4. SAMPLE CALCULATION

- 4.1 Exhaust emissions from a gasoline vehicle are collected in three dilute exhaust sample bags and one dilution air (background) sample bag during the FTP. Gas chromatography is used to determine the benzene concentration of each bag sample. Calculate the weighted benzene mass emissions based on the following data:

Test Phase	HC _e (ppbC)	HC _d (ppbC)	FID THC _e (ppmC)	CH _{4e} (ppmC)	CO _{2e} (%)	CO _{em} (ppm)	R _a (%)	VMIX (ft ³)	D _{phasen} (mile)
1	500	25	98	6	1.20	280	28	2846	3.584
2	100	25	22	4	0.95	87	25	4854	3.842
3	120	25	29	5	1.07	101	24	2840	3.586

For Phase 1:

$$\text{DF} = 13.47 / [\text{CO}_{2e} + (\text{NMHC}_e + \text{CH}_{4e} + \text{CO}_e) * 10^{-4}]$$

(see section 6, DF Calc.)

$$\begin{aligned}\text{NMHC}_e &= \text{FID THC}_e - (r_{\text{CH}_4} * \text{CH}_{4e}) \\ &= 98 \text{ ppmC} - (1.04 * 6 \text{ ppmC}) \\ &= 92 \text{ ppmC}\end{aligned}$$

$$\text{CO} = (1 - (0.01 + 0.005 * \text{HCR}) * \text{CO}_{2e} - 0.000323 * R_a) * \text{CO}_{em}$$

NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e.

$$\begin{aligned}&= (1 - (0.01925) * 1.2\% - 0.000323 * 28\%) * 280 \text{ ppm} \\ &= 271 \text{ ppm}\end{aligned}$$

$$\begin{aligned}\text{DF} &= 13.47 / [1.2\% + (92 \text{ ppmC} + 6 \text{ ppmC} + 271 \text{ ppm}) * 10^{-4}] \\ &= 10.89\end{aligned}$$

$$\begin{aligned}\text{HC}_{\text{conc}} &= \text{HC}_e - (\text{HC}_d * (1 - (1 / \text{DF}))) \\ &= 500 \text{ ppbC} - (25 \text{ ppbC} * (1 - (1 / 10.89))) \\ &= 477 \text{ ppbC}\end{aligned}$$

$$\begin{aligned}\text{Mol. Wt. of C}_6\text{H}_6 &= (6 * 12.01115) + (6 * 1.00797) \\ &= 78.11472 \text{ g/mole}\end{aligned}$$

$$\begin{aligned}\text{HC}_{\text{dens}} &= (\text{Mol. Wt.} * \text{conversion of liter to ft}^3) / (\text{Mol. Vol.}) \\ &= (78.11472 \text{ g/mole} * 28.316 \text{ liter/ft}^3) / 24.055 \text{ liter/mole} \\ &= 91.952 \text{ g/ft}^3\end{aligned}$$

$$\text{HC}_{\text{mass n}} = (\text{HC}_{\text{conc}} * \text{HC}_{\text{dens}} * \text{VMIX} * 10^{-6}) / (\text{Carbon No.})$$

$$\begin{aligned}\text{HC}_{\text{mass 1}} &= (477 \text{ ppbC} * 91.952 \text{ g/ft}^3 * 2846 \text{ ft}^3 * 10^{-6}) / 6 \\ &= 20.8 \text{ mg}\end{aligned}$$

$$\text{Similarly, for Phase 2:} \quad \text{HC}_{\text{mass}} = 5.7 \text{ mg}$$

$$\text{and for Phase 3:} \quad \text{HC}_{\text{mass}} = 4.2 \text{ mg}$$

Therefore,

$$\text{HC}_{\text{wm}} = 0.43 * \frac{(\text{HC}_{\text{mass 1}} + \text{HC}_{\text{mass 2}})}{(\text{D}_{\text{phase 1}} + \text{D}_{\text{phase 2}})} + 0.57 * \frac{(\text{HC}_{\text{mass 3}} + \text{HC}_{\text{mass 2}})}{(\text{D}_{\text{phase 3}} + \text{D}_{\text{phase 2}})}$$

$$HC_{wm} = 0.43 * \frac{(20.8 \text{ mg} + 5.7 \text{ mg})}{(3.584 \text{ mile} + 3.842 \text{ mile})} + 0.57 * \frac{(4.2 \text{ mg} + 5.7 \text{ mg})}{(3.586 \text{ mile} + 3.842 \text{ mile})}$$

$$HC_{wm} = 2.3 \text{ mg/mile (benzene weighted mass emissions)}$$

4. ALCOHOL MASS EMISSIONS CALCULATION

1. INTRODUCTION

- 1.1 Vehicular emissions are measured according to the ~~Federal Test Procedure (FTP)~~[Ref. 1] (1). For each of the three phases of the FTP, a set of two impingers is used to collect alcohol emissions in the dilute exhaust. A fourth set of two impingers is used to collect a composite dilution air (background) alcohol sample from all three phases of the FTP. All impingers are analyzed according to Method No. 1001 to determine the alcohol concentration in each impinger. The measured alcohol concentrations are used in the following equations to calculate the weighted mass emissions of alcohol compounds.

2. ALCOHOL MASS EMISSIONS CALCULATION PER TEST PHASE

$$2.1 \quad ROH_{\text{mass } n} = (ROH_{\text{conc}} * ROH_{\text{dens}} * VMIX * 10^{-6}) / (\text{Carbon No.})$$

$$2.2 \quad ROH_{\text{conc}} = ROH_e - (ROH_d * (1 - (1 / DF)))$$

NOTE: If ROH_{conc} is calculated to be less than zero, then $ROH_{\text{conc}} = 0$.

$$2.3 \quad ROH_e = (Imass_e / Ivol_e) * (\text{Mol. Vol.} / \text{Mol. Wt.})$$

$$2.4 \quad Imass_e = (Iconc_{e1} + Iconc_{e2}) * Dens_{ROH} * Ivol_r$$

$$2.5 \quad Ivol_e = \frac{Ivol_{em} * (\text{Itemp}_e / 293.16^\circ \text{K}) * (760 \text{ mm Hg} / P_B)}{(293.16^\circ \text{K} / \text{Itemp}_e) * (P_B / 760 \text{ mm Hg})}$$

$$2.6 \quad ROH_d = (Imass_d / Ivol_d) * (\text{Mol. Vol.} / \text{Mol. Wt.})$$

$$2.7 \quad Imass_d = (Iconc_{d1} + Iconc_{d2}) * Dens_{ROH} * Ivol_r$$

$$2.8 \quad Ivol_d = \frac{Ivol_{dm} * (\text{Itemp}_d / 293.16^\circ \text{K}) * (760 \text{ mm Hg} / P_B)}{(293.16^\circ \text{K} / \text{Itemp}_d) * (P_B / 760 \text{ mm Hg})}$$

3. WEIGHTED ALCOHOL MASS EMISSIONS CALCULATION

$$ROH_{\text{wm}} = 0.43 * \frac{(ROH_{\text{mass } 1} + ROH_{\text{mass } 2})}{(D_{\text{phase } 1} + D_{\text{phase } 2})} + 0.57 * \frac{(ROH_{\text{mass } 3} + ROH_{\text{mass } 2})}{(D_{\text{phase } 3} + D_{\text{phase } 2})}$$

4. SAMPLE CALCULATION

- 4.1 Alcohol emissions from an M85 fueled vehicle are collected in three sets of dilute exhaust impingers and one set of dilution air impingers during the FTP. Gas chromatography is used to determine the methanol concentration in each impinger. Calculate the weighted methanol mass emissions based on the following data:

Test Phase	Ivol _r (mL)	Iconc _{e1} (ppmC)	Iconc _{e2} (ppmC)	Ivol _{em} (liter)	Iconc _{d1} (ppmC)	Iconc _{d2} (ppmC)	Ivol _{dm} (liter)	Itemp _e (°K)	Itemp _d (°K)
1	15	2.24	0.05	3.90	0.07	0.01	13.50	295	294
2	15	0.29	0.06	6.50	0.07	0.01	13.50	297	294
3	15	0.32	0.02	4.00	0.07	0.01	13.50	298	294

Test Phase	FID THC _e (ppmC)	CH _{4e} (ppmC)	CO _{2e} (%)	CO _{em} (ppm)	R _a (%)	VMIX (ft ³)	D _{phase n} (mile)	P _B (mmHg)	HCHO _e (ppm)
1	82	9	1.5	250	30	2834	3.581	760	0.81
2	19	5	0.7	20	32	4862	3.845	760	0.09
3	22	6	0.8	32	29	2835	3.583	760	0.10

For Phase 1:

$$\begin{aligned}
 \text{Imass}_e &= (\text{Iconc}_{e1} + \text{Iconc}_{e2}) * \text{Dens}_{\text{ROH}} * \text{Ivol}_r \\
 &= (2.24 \text{ ppmC} + 0.05 \text{ ppmC}) * 0.7914 \text{ g/mL} * 15 \text{ mL} * 10^6 \mu\text{g/g} \\
 &= 27.2 \mu\text{g}
 \end{aligned}$$

$$\begin{aligned}
 \text{Mol. Wt. of CH}_3\text{OH} &= (1 * 12.01115) + (4 * 1.00797) + (1 * 15.9994) \\
 &= 32.0428 \text{ g/mole}
 \end{aligned}$$

$$\begin{aligned}
 \text{Ivol}_e &= \text{Ivol}_{em} * \frac{(\text{Itemp}_e / 293.16^\circ \text{K}) * (760 \text{ mm Hg} / P_B)}{(293/16^\circ \text{K} / \text{Itemp}_e) * (P_B / 760 \text{ mm Hg})} \\
 &= 3.90 \text{ liter} * \frac{(295^\circ \text{K} / 293.16^\circ \text{K}) * (293.16^\circ \text{K} / 295^\circ \text{K})}{(760 \text{ mm Hg} / 760 \text{ mm Hg})} * \\
 &= \underline{3.92} \underline{3.88} \text{ liter}
 \end{aligned}$$

$$\begin{aligned}
 \text{ROH}_e &= (\text{Imass}_e / \text{Ivol}_e) * (\text{Mol. Vol.} / \text{Mol. Wt.}) \\
 &= (27.2 * 10^{-6} \text{ g} / \underline{3.92} \underline{3.88} \text{ liter}) * (24.055 \text{ liter/mole} / 32.0428 \text{ g/mole}) \\
 &= \underline{5.20} \underline{5.27} \text{ ppmC}
 \end{aligned}$$

$$\begin{aligned}\text{Imass}_d &= (\text{Iconc}_{d1} + \text{Iconc}_{d2}) * \text{Dens}_{\text{ROH}} * \text{Ivol}_r \\ &= (0.07 \text{ ppmC} + 0.01 \text{ ppmC}) * 0.7914 \text{ g/ml} * 15 \text{ ml} * 10^6 \mu\text{g/g} \\ &= 0.95 \mu\text{g}\end{aligned}$$

$$\begin{aligned}\text{Ivol}_d &= \text{Ivol}_{dm} * (\text{Itemp}_d / 293.16^\circ \text{K}) * (760 \text{ mm Hg} / P_B) \\ &\quad (293.16^\circ \text{K} / \text{Itemp}_d) * (P_B / 760 \text{ mm Hg}) \\ &= 13.50 \text{ liter} * (\cancel{294^\circ \text{K}} / 293.16^\circ \text{K}) * (293.16^\circ \text{K} / 294^\circ \text{K}) * \\ &\quad (760 \text{ mm Hg} / 760 \text{ mm Hg}) \\ &= \cancel{13.54} \text{ 13.46 liter}\end{aligned}$$

$$\begin{aligned}\text{ROH}_d &= (\text{Imass}_d / \text{Ivol}_d) * (\text{Mol. Vol.} / \text{Mol. Wt.}) \\ &= (0.95 * 10^{-6} \text{ g} / \cancel{13.54} \text{ 13.46 liter}) * (24.055 \text{ liter/mole} / 32.0428 \text{ g/mole}) \\ &= 0.05 \text{ ppmC}\end{aligned}$$

$$\text{DF} = 12.02 / [\text{CO}_{2e} + (\text{NMHC}_e + \text{CH}_{4e} + \text{CO}_e + \text{ROH}_e + \text{HCHO}_e) * 10^{-4}] \text{ (see section 6, DF Calc.)}$$

$$\begin{aligned}\text{NMHC}_e &= \text{FID THC}_e - (r_{\text{CH}_4} * \text{CH}_{4e}) - (r_{\text{CH}_3\text{OH}} * \text{ROH}_e) \\ &= 82 \text{ ppmC} - (1.04 * 9 \text{ ppmC}) - (0.66 * 5.27 \text{ ppmC}) \\ &= \cancel{73} \text{ 69 ppmC}\end{aligned}$$

$$\text{CO}_e = (1 - (0.01 + 0.005 * \text{HCR})) * \text{CO}_{2e} - 0.000323 * R_a * \text{CO}_{em}$$

NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e.

$$\begin{aligned}&= (1 - (0.02705) * 1.5\% - 0.000323 * 30\%) * 250 \text{ ppm} \\ &= 237 \text{ ppm}\end{aligned}$$

$$\begin{aligned}\text{DF} &= \frac{12.02}{1.5\% + (\cancel{73} \text{ 69 ppmC} + 9 \text{ ppmC} + 237 \text{ ppmC} + \cancel{5.30} \text{ 5.27 ppmC} + 0.81 \text{ ppm}) * 10^{-4}} \\ &= \cancel{7.85} \text{ 7.84}\end{aligned}$$

$$\begin{aligned}\text{ROH}_{\text{conc}} &= \text{ROH}_e - (\text{ROH}_d * (1 - (1 / \text{DF}))) \\ &= \cancel{5.20} \text{ 5.27 ppmC} - (0.05 \text{ ppmC} * (1 - (1 / 7.84))) \\ &= \cancel{5.15} \text{ 5.23 ppmC}\end{aligned}$$

$$\begin{aligned}\text{ROH}_{\text{dens}} &= (\text{Mol. Wt.} * \text{conversion of liter to ft}^3) / (\text{Mol. Vol.}) \\ &= (32.0428 \text{ g/mole} * 28.316 \text{ liter/ft}^3) / 24.055 \text{ liter/mole} \\ &= 37.719 \text{ g/ft}^3\end{aligned}$$

$$\begin{aligned}\text{ROH}_{\text{mass n}} &= (\text{ROH}_{\text{conc}} * \text{ROH}_{\text{dens}} * \text{VMIX} * 10^{-6}) / (\text{Carbon No.}) \\ \text{ROH}_{\text{mass l}} &= (\cancel{5.15} \text{ 5.23 ppmC} * 37.719 \text{ g/ft}^3 * 2834 \text{ ft}^3 * 10^{-6}) / 1 \\ &= \cancel{0.55} \text{ 0.56 g}\end{aligned}$$

Similarly, for Phase 2:

$$\text{ROH}_{\text{mass } 2} = 0.08 \text{ g}$$

and for Phase 3:

$$\text{ROH}_{\text{mass } 3} = \cancel{0.07} \underline{0.08} \text{ g}$$

Therefore,

$$\text{ROH}_{\text{wm}} = 0.43 * \frac{(\text{ROH}_{\text{mass } 1} + \text{ROH}_{\text{mass } 2})}{(\text{D}_{\text{phase } 1} + \text{D}_{\text{phase } 2})} + 0.57 * \frac{(\text{ROH}_{\text{mass } 3} + \text{ROH}_{\text{mass } 2})}{(\text{D}_{\text{phase } 3} + \text{D}_{\text{phase } 2})}$$

$$\text{ROH}_{\text{wm}} = 0.43 * \frac{(\cancel{0.55} \underline{0.56} \text{ mg} + 0.08 \text{ mg})}{(3.581 \text{ mile} + 3.845 \text{ mile})} + 0.57 * \frac{(\cancel{0.07} \underline{0.08} \text{ mg} + 0.08 \text{ mg})}{(3.583 \text{ mile} + 3.845 \text{ mile})}$$

$$\text{ROH}_{\text{wm}} = 0.05 \text{ g (methanol weighted mass emissions)}$$

5. CARBONYL MASS EMISSIONS CALCULATIONS

1. INTRODUCTION

- 1.1 Vehicular emissions are measured according to the ~~Federal Test Procedure~~ (FTP) [Ref. 1] (4). For each of the three phases of the FTP, a set of two impingers (or cartridges) is used to collect carbonyl emissions in the dilute exhaust. A fourth set of two impingers (or cartridges) is used to collect a composite dilution air (background) carbonyl sample from all three phases of the FTP. All impingers (or cartridges) are analyzed according to Method No. 1004 to determine the mass of individual carbonyl compounds in each impinger (or cartridge). The measured carbonyl masses are used in the following equations to calculate the weighted mass emissions of each carbonyl compound.

2. CARBONYL MASS EMISSIONS CALCULATION PER TEST PHASE

- 2.1 $RHO_{mass\ n} = (RHO_{conc} * RHO_{dens} * VMIX * 10^{-6})$
- 2.2 $RHO_{conc} = RHO_e - (RHO_d * (1 - (1 / DF)))$
 NOTE: If RHO_{conc} is calculated to be less than zero, then $RHO_{conc} = 0$.
- 2.3 $RHO_e = (Imass_e / Ivol_e) * (Mol. Vol. / Mol. Wt.)$
- 2.4 $Ivol_e = \frac{Ivol_{em} * (\cancel{Itemp_e - 293.16^\circ K}) * (\cancel{760\ mm\ Hg} / P_B)}{(293.16^\circ K / Itemp_e) * (P_B / 760\ mm\ Hg)}$
- 2.5 $RHO_d = (Imass_d / Ivol_d) * (Mol. Vol. / Mol. Wt.)$
- 2.6 $Ivol_d = \frac{Ivol_{dm} * (\cancel{Itemp_d - 293.16^\circ K}) * (\cancel{760\ mm\ Hg} / P_B)}{(293.16^\circ K / Itemp_d) * (P_B / 760\ mm\ Hg)}$

3. WEIGHTED CARBONYL MASS EMISSIONS CALCULATION

$$RHO_{wm} = 0.43 * \frac{(RHO_{mass\ 1} + RHO_{mass\ 2})}{(D_{phase\ 1} + D_{phase\ 2})} + 0.57 * \frac{(RHO_{mass\ 3} + RHO_{mass\ 2})}{(D_{phase\ 3} + D_{phase\ 2})}$$

4. SAMPLE CALCULATION

- 4.1 Carbonyl emissions from a ~~compressed natural gas (CNG)~~ vehicle are collected in three sets of dilute exhaust impingers and one set of dilution air impingers during the FTP. ~~High performance liquid chromatography~~ HPLC is used to determine the formaldehyde mass in each impinger. Calculate the weighted formaldehyde mass emissions based on the following data:

Test Phase	Ivol _r (mL)	Imass _e (μg)	Ivol _{em} (liter)	Imass _d (μg)	Ivol _{dm} (liter)	Itemp _e (°K)	Itemp _d (°K)
1	15	2.45	8.49	0.17	31.57	295	292
2	15	0.76	14.55	0.17	31.57	298	292
3	15	0.64	4.00	0.17	31.57	298	292

Test Phase	FID THC _e (ppmC)	CH _{4e} (ppmC)	CO _{2e} (%)	CO _{em} (ppm)	R _a (%)	VMIX (ft ³)	D _{phase n} (mile)	P _B (mmHg)
1	132	108	0.9	8	68	2866	3.581	760
2	4	3	0.1	4	67	4841	3.845	760
3	22	9	0.5	5	65	2837	3.583	760

For Phase 1:

$$\begin{aligned} \text{Mol. Wt. of HCHO} &= (1 * 12.01115) + (2 * 1.00797) + (1 * 15.9994) \\ &= 30.0268 \text{ g/mole} \end{aligned}$$

$$\begin{aligned} \text{Ivol}_e &= \text{Ivol}_{em} * \frac{(\text{Itemp}_e - 293.16^\circ \text{K}) * (760 \text{ mm Hg} / P_B)}{(293.16^\circ \text{K} / \text{Itemp}_e) * (P_B / 760 \text{ mm Hg})} \\ &= 8.49 \text{ liter} * \frac{(295^\circ \text{K} - 293.16^\circ \text{K}) * (293.16^\circ \text{K} / 295^\circ \text{K})}{(760 \text{ mm Hg} / 760 \text{ mm Hg})} \\ &= 8.54 \text{ } \underline{8.44} \text{ liter} \end{aligned}$$

$$\begin{aligned} \text{RHO}_e &= (\text{Imass}_e / \text{Ivol}_e) * (\text{Mol. Vol.} / \text{Mol. Wt.}) \\ &= (2.45 * 10^{-6} \text{ g} / 8.54 \text{ } \underline{8.44} \text{ liter}) * (24.055 \text{ liter/mole} / 30.0268 \text{ g/mole}) \\ &= 230 \text{ } \underline{233} \text{ ppb} \end{aligned}$$

$$\begin{aligned} \text{Ivol}_d &= \text{Ivol}_{dm} * \frac{(\text{Itemp}_d - 293.16^\circ \text{K}) * (760 \text{ mm Hg} / P_B)}{(293.16^\circ \text{K} / \text{Itemp}_d) * (P_B / 760 \text{ mm Hg})} \\ &= 31.57 \text{ liter} * \frac{(292^\circ \text{K} - 293.16^\circ \text{K}) * (293.16^\circ \text{K} / 292^\circ \text{K})}{(760 \text{ mm Hg} / 760 \text{ mm Hg})} \\ &= 31.45 \text{ } \underline{31.70} \text{ liter} \end{aligned}$$

$$\begin{aligned} \text{RHO}_d &= (\text{Imass}_d / \text{Ivol}_d) * (\text{Mol. Vol.} / \text{Mol. Wt.}) \\ &= (0.17 * 10^{-6} \text{ g} / 31.45 \text{ } \underline{31.70} \text{ liter}) * (24.055 \text{ liter/mole} / 30.0268 \text{ g/mole}) \\ &= 4 \text{ ppb} \end{aligned}$$

$$DF = 9.77 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e) * 10^{-4}] \text{ (see section 6, DF Calc.)}$$

$$\begin{aligned} NMHC_e &= FID\ THC_e - (r_{CH_4} * CH_{4e}) \\ &= 132\ ppmC - (1.04 * 108\ ppmC) \\ &= 20\ ppmC \end{aligned}$$

$$CO_e = (1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a) * CO_{em}$$

NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e.

$$\begin{aligned} &= (1 - 0.02900 * 0.02890 * 0.9\% - 0.000323 * 68\%) * 8\ ppm \\ &= 7.6\ ppm \end{aligned}$$

$$\begin{aligned} DF &= 9.77 / [0.9\% + (20\ ppmC + 108\ ppmC + 7.6\ ppm) * 10^{-4}] \\ &= 10.69 \end{aligned}$$

$$\begin{aligned} RHO_{conc} &= RHO_e - (RHO_d * (1 - (1 / DF))) \\ &= 230\ 233\ ppb - (4.33\ 4\ ppb * (1 - (1 / 10.69))) \\ &= 226\ 229\ ppb \end{aligned}$$

$$\begin{aligned} RHO_{dens} &= (Mol.\ Wt. * \text{conversion of liter to ft}^3) / (Mol.\ Vol.) \\ &= (30.0268\ g/mole * 28.316\ liter/ft^3) / 24.055\ liter/mole \\ &= 35.35\ g/ft^3 \end{aligned}$$

$$\begin{aligned} RHO_{mass\ n} &= (RHO_{conc} * RHO_{dens} * VMIX * 10^{-6}) \\ RHO_{mass\ 1} &= (226\ 229\ ppb * 35.35\ g/ft^3 * 2866\ ft^3 * 10^{-6}) \\ &= 22.9\ 23.2\ mg \end{aligned}$$

Similarly, for Phase 2:

$$RHO_{mass\ 2} = 6.3\ 6.6\ mg$$

and for Phase 3:

$$RHO_{mass\ 3} = 12.2\ 12.7\ mg$$

Therefore,

$$\begin{aligned} RHO_{wm} &= 0.43 * \frac{(RHO_{mass\ 1} + RHO_{mass\ 2})}{(D_{phase\ 1} + D_{phase\ 2})} + 0.57 * \frac{(RHO_{mass\ 3} + RHO_{mass\ 2})}{(D_{phase\ 3} + D_{phase\ 2})} \\ RHO_{wm} &= 0.43 * \frac{(22.9\ 23.2\ mg + 6.3\ 6.6\ mg)}{(3.581\ mile + 3.845\ mile)} + 0.57 * \frac{(12.2\ 12.7\ mg + 6.3\ 6.6\ mg)}{(3.583\ mile + 3.845\ mile)} \\ RHO_{wm} &= 3.1\ 3.2\ g\ mg/mi \text{ (formaldehyde weighted mass emissions)} \end{aligned}$$

6. DILUTION FACTOR CALCULATION

1. DILUTION FACTORS

1.1 For Non-Alcohol Fueled Vehicles:

$$1.1.1 \quad DF = \frac{100 * \frac{x}{x + y/2 + 3.76 * (x + y/4 - z/2)}}{\frac{CO_{2e} + (NMHC_e + CH_{4e} + CO_e) * 10^{-4}}{(where \text{ fuel composition is } C_xH_yO_z \text{ as measured for the fuel used.})}}$$

$$1.1.2 \quad CO_e = (1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a) * CO_{em}$$

NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e.

a) For gasoline, CH_{1.85}, where x = 1, y = 1.85, and z = 0:

$$DF = 13.47 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e) * 10^{-4}]$$

$$CO_e = (1 - 0.01925 * CO_{2e} - 0.000323 * R_a) * CO_{em}$$

b) For Phase 2 gasoline, CH_{1.94}, where x = 1, y = 1.94 and z = 0.017,

$$DF = 13.29 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e) * 10^{-4}]$$

$$CO_e = (1 - 0.01970 * CO_{2e} - 0.000323 * R_a) * CO_{em}$$

~~b~~c) For LPG, CH_{~~2.66~~ 2.64}, where x = 1, y = ~~2.66~~ 2.64, z = 0:

$$DF = ~~11.64~~ 11.68 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e) * 10^{-4}]$$

$$CO_e = (1 - ~~0.02330~~ 0.02320 * CO_{2e} - 0.000323 * R_a) * CO_{em}$$

~~c~~d) For CNG, CH_{~~3.80~~ 3.78}, where x = 1, y = ~~3.80~~ 3.78, and z = ~~0.016~~:

$$DF = ~~9.77~~ 9.83 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e) * 10^{-4}]$$

$$CO_e = (1 - ~~0.02900~~ 0.02890 * CO_{2e} - 0.000323 * R_a) * CO_{em}$$

1.2 For Alcohol Fueled Vehicles:

$$1.2.1 \quad DF = \frac{100 * \frac{x}{x + y/2 + 3.76 * (x + y/4 - z/2)}}{\frac{CO_{2e} + (NMHC_e + CH_{4e} + CO_e + ROH_e + HCHO_e) * 10^{-4}}{(where \text{ fuel composition is } C_xH_yO_z \text{ as measured for the fuel used.})}}$$

1.2.2 $CO_e = (1 - (0.01 + 0.005 * HCR) * CO_{2e} - 0.000323 * R_a) * CO_{em}$

NOTE: If a CO instrument which meets the criteria specified in CFR 40, 86.111 is used and the conditioning column has been deleted, CO_{em} must be substituted directly for CO_e .

- a) For M100 (100% methanol), CH_3OH , where $x = 1$, $y = 4$, and $z = 1$:
 $DF = 11.57 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e + ROH_e + HCHO_e) * 10^{-4}]$
 $CO_e = (1 - 0.03000 * CO_{2e} - 0.000323 * R_a) * CO_{em}$
- b) For M85 (85% methanol, 15% indolene), $CH_{3.41}O_{0.72}$, where $x = 1$, $y = 3.41$, and $z = 0.72$:
 $DF = 12.02 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e + ROH_e + HCHO_e) * 10^{-4}]$
 $CO_e = (1 - 0.02705 * CO_{2e} - 0.000323 * R_a) * CO_{em}$
- c) For E100 (100% ethanol), C_2H_5OH , where $x = 1$, $y = 3$, and $z = 0.5$:
 $DF = 12.29 / [CO_{2e} + (NMHC_e + CH_{4e} + CO_e + ROH_e + HCHO_e) * 10^{-4}]$
 $CO_e = (1 - 0.02500 * CO_{2e} - 0.000323 * R_a) * CO_{em}$

Attachment APPENDIX 1LIST OF COMPOUNDS

<u>CAS #</u>	<u>COMPOUND</u>	<u>MIR</u>
<u>Alcohols</u>		
<u>00067-56-1</u>	<u>methanol</u>	<u>0.56</u>
<u>00064-17-5</u>	<u>ethanol</u>	<u>1.34</u>
Light End and Mid-Range Hydrocarbons (Listed in approximate elution order)		
00074-85-1	ethene	<u>7.29</u>
00074-86-2	ethyne	<u>0.50</u>
00074-84-0	ethane	<u>0.25</u>
00115-07-1	propene	<u>9.40</u>
00074-98-6	propane	<u>0.48</u>
00463-49-0	<u>1,2-propadiene</u>	<u>10.89</u>
00074-99-7	1-propyne	<u>4.10</u>
00075-28-5	<u>2-methylpropane</u>	<u>1.21</u>
00115-11-7	2-methylpropene	<u>5.31</u>
00106-98-9	1-butene	<u>8.91</u>
00106-99-0	1,3-butadiene	<u>10.89</u>
00106-97-8	n-butane	<u>1.02</u>
00624-64-6	trans-2-butene	<u>9.94</u>
00463-82-1	2,2-dimethylpropane	<u>0.37</u>
00107-00-6	1-butyne	<u>9.24</u>
00590-18-1	cis-2-butene	<u>9.94</u>
00563-45-1	3-methyl-1-butene	<u>6.22</u>
00078-78-4	2-methylbutane	<u>1.38</u>
00503-17-3	2-butyne	<u>9.24</u>
00109-67-1	1-pentene	<u>6.22</u>
00563-46-2	2-methyl-1-butene	<u>4.90</u>
00109-66-0	n-pentane	<u>1.04</u>
00078-79-5	2-methyl <u>2-methyl-1,3-butadiene</u>	<u>9.08</u>
00646-04-8	trans-2-pentene	<u>8.80</u>
00558-37-2	3,3-dimethyl-1-butene	<u>4.42</u>
00627-20-3	cis-2-pentene	<u>8.80</u>
<u>00689-97-4</u>	<u>1-buten-3-yne</u>	<u>9.24</u>
00513-35-9	2-methyl-2-butene	<u>6.41</u>
00542-92-7	<u>1,3-cyclopentadiene</u>	<u>7.66</u>
00075-83-2	2,2-dimethylbutane	<u>0.82</u>
00142-29-0	cyclopentene	<u>7.66</u>
00691-37-2	4-methyl-1-pentene	<u>4.42</u>

CAS #	COMPOUND	MIR
00760-20-3	3-methyl-1-pentene	<u>4.42</u>
00287-92-3	cyclopentane	<u>2.38</u>
00079-29-8	2,3-dimethylbutane	<u>1.07</u>
01634-04-4	1-methyl-tert-butyl-ether	<u>0.62</u>
00691-38-3	4-methyl-cis-2-pentene	<u>6.69</u>
00107-83-5	2-methylpentane	<u>1.53</u>
00674-76-0	4-methyl-trans-2-pentene	<u>6.69</u>
00096-14-0	3-methylpentane	<u>1.52</u>
00763-29-1	2-methyl-1-pentene	<u>4.42</u>
00592-41-6	1-hexene	<u>4.42</u>
00110-54-3	n-hexane	<u>0.98</u>
13269-52-8	trans-3-hexene	<u>6.69</u>
07642-09-3	cis-3-hexene	<u>6.69</u>
04050-45-7	trans-2-hexene	<u>6.69</u>
00616-12-6	3-methyl-trans-2-pentene	<u>6.69</u>
00625-27-4	2-methyl-2-pentene	<u>6.69</u>
01120-62-3	3-methylcyclopentene	<u>5.65</u>
07688-21-3	cis-2-hexene	<u>6.69</u>
00637-92-3	1-ethyl-tert-butyl-ether	<u>1.98</u>
00922-62-3	3-methyl-cis-2-pentene	<u>6.69</u>
00590-35-2	2,2-dimethylhexane	<u>1.40</u>
00096-37-7	methylcyclopentane	<u>2.82</u>
00108-08-7	2,4-dimethylpentane	<u>1.78</u>
00464-06-2	2,2,3-trimethylbutane	<u>1.32</u>
07385-78-6	3,4-dimethyl-1-pentene	<u>3.48</u>
00693-89-0	1-methylcyclopentene	<u>7.66</u>
00071-43-2	benzene	<u>0.42</u>
03404-61-3	3-methyl-1-hexene	<u>3.48</u>
00562-049-2	3,3-dimethylpentane	<u>0.71</u>
00110-82-7	cyclohexane	<u>1.28</u>
00591-76-4	2-methylhexane	<u>1.08</u>
00565-59-3	2,3-dimethylpentane	<u>1.51</u>
00110-83-8	cyclohexene	<u>5.67</u>
00589-34-4	3-methylhexane	<u>1.40</u>
02532-58-3	cis-1,3-dimethylcyclopentane	<u>2.55</u>
00617-78-7	3-ethylpentane	<u>1.40</u>
00822-50-4	trans-1,2-dimethylcyclopentane	<u>1.85</u>
00592-76-7	1-heptene	<u>3.48</u>
00540-84-1	2,2,4-trimethylpentane	<u>0.93</u>
14686-14-7	trans-3-heptene	<u>5.53</u>
00142-82-5	n-heptane	<u>0.81</u>
02738-19-4	2-methyl-2-hexene	<u>5.53</u>

CAS #	COMPOUND	MIR
03899-36-3	3-methyl-trans-3-hexene	<u>5.53</u>
14686-13-6	trans-2-heptene	<u>5.53</u>
00816-79-5	3-ethyl-cis-2-pentene	<u>5.53</u>
00107-39-1	2,4,4-trimethyl-1-pentene	<u>2.69</u>
10574-37-5	2,3-dimethyl-2-pentene	<u>5.53</u>
06443-92-1	cis-2-heptene	<u>5.53</u>
00108-87-2	methylcyclohexane	<u>1.85</u>
00590-73-8	2,2-dimethylhexane	<u>1.20</u>
00107-40-4	2,4,4-trimethyl-2-pentene	<u>5.29</u>
<u>01640-89-7</u>	<u>ethylcyclopentane</u>	<u>2.31</u>
00592-13-2	2,5-dimethylhexane	<u>1.63</u>
00589-43-5	2,4-dimethylhexane	<u>1.50</u>
00563-16-6	3,3-dimethylhexane	<u>1.20</u>
00565-75-3	2,3,4-trimethylpentane	<u>1.60</u>
00560-21-4	2,3,3-trimethylpentane	<u>1.20</u>
00108-88-3	toluene	<u>2.73</u>
00584-94-1	2,3-dimethylhexane	<u>1.32</u>
00592-27-8	2-methylheptane	<u>0.96</u>
00589-53-7	4-methylheptane	<u>1.20</u>
00589-81-1	3-methylheptane	<u>0.99</u>
15890-40-1	1-cis-2-trans(1a,2a,3b)-1,2,3-trimethylcyclopentane	<u>1.94</u>
00638-04-0	cis-1,3-dimethylcyclohexane	<u>1.94</u>
02207-04-7	trans-1,4-dimethylcyclohexane	<u>1.94</u>
03522-94-9	2,2,5-trimethylhexane	<u>0.97</u>
<u>16747-50-5</u>	<u>cis-1-methyl-3-ethylcyclopentane</u>	<u>1.94</u>
00111-66-0	1-octene	<u>2.69</u>
14850-23-8	trans-4-octene	<u>5.29</u>
00111-65-9	n-octane	<u>0.61</u>
13389-42-9	trans-2-octene	<u>5.29</u>
02207-03-6	trans-1,3-dimethylcyclohexane	<u>1.94</u>
07642-04-8	cis-2-octene	<u>5.29</u>
01069-53-0	2,3,5-trimethylhexane	<u>1.14</u>
02213-23-2	2,4-dimethylheptane	<u>1.34</u>
02207-01-4	cis-1,2-dimethylcyclohexane	<u>1.94</u>
01678-91-7	ethylcyclohexane	<u>1.94</u>
00926-82-9	3,5-dimethylheptane	<u>1.14</u>
00100-41-4	ethylbenzene	<u>2.70</u>
03074-71-3 2	2,3-dimethylheptane	<u>1.14</u>
00108-38-3	m-&p-xylene	<u>7.64</u>
<u>02216-34-4</u>	<u>4-methyloctane</u>	<u>1.14</u>
03221-61-2	2-methyloctane	<u>1.14</u>
02216-33-3	3-methyloctane	<u>1.14</u>

CAS #	COMPOUND	MIR
00100-42-5	styrene(ethenylbenzene)	<u>2.22</u>
00095-47-6	o-xylene	<u>6.46</u>
00124-11-8	1-nonene	<u>2.23</u>
00111-84-2	n-nonane	<u>0.54</u>
00098-82-8	(1-methylethyl)benzene	<u>2.24</u>
15869-87-1	2,2-dimethyloctane	<u>1.01</u>
04032-94-4	2,4-dimethyloctane	<u>1.01</u>
00103-65-1	n-propylbenzene	<u>2.12</u>
00620-14-4	1-methyl-3-ethylbenzene	<u>7.20</u>
006220-96-8	1-methyl-4-ethylbenzene	<u>7.20</u>
00108-67-8	1,3,5-trimethylbenzene	<u>10.12</u>
00611-14-3	1-methyl-2-ethylbenzene	<u>7.20</u>
00095-63-6	1,2,4-trimethylbenzene	<u>8.83</u>
00124-18-5	n-decane	<u>0.47</u>
00538-93-2	(2-methylpropyl)benzene	<u>1.87</u>
00135-98-8	(1-methylpropyl)benzene	<u>1.89</u>
00535-77-3	1-methyl-3-(1-methylethyl)benzene	<u>6.45</u>
005726-73-8	1,2,3-trimethylbenzene	<u>8.85</u>
00099-87-6	1-methyl-4-(1-methylethyl)benzene	<u>6.45</u>
00496-11-7	2,3-dihydroindene(indan)	<u>1.06</u>
00527-84-4	1-methyl-2-(1-methylethyl)benzene	<u>6.45</u>
00141-93-5	1,3-diethylbenzene	<u>6.45</u>
00105-05-5	1,4-diethylbenzene	<u>6.45</u>
01074-43-7	1-methyl-3-n-propylbenzene	<u>6.45</u>
01074-55-1	1-methyl-4-n-propylbenzene	<u>6.45</u>
00135-01-3	1,2-diethylbenzene	<u>6.45</u>
01074-17-5	1-methyl-2-n-propylbenzene	<u>6.45</u>
01758-88-9	1,4-dimethyl-2-ethylbenzene	<u>9.07</u>
00874-41-9	1,3-dimethyl-4-ethylbenzene	<u>9.07</u>
00934-80-5	1,2-dimethyl-4-ethylbenzene	<u>9.07</u>
02870-040-4	1,3-dimethyl-2-ethylbenzene	<u>9.07</u>
01120-21-4	n-undecane(hendecane)	<u>0.42</u>
00933-98-2	1,2-dimethyl-3-ethylbenzene	<u>9.07</u>
00095-93-2	1,2,4,5-tetramethylbenzene	<u>9.07</u>
03968-85-2	(2-methylbutyl)benzene	<u>1.70</u>
00527-53-7	1,2,3,5-tetramethylbenzene	<u>9.07</u>
27138-21-2 01074-92-6	1-(1,1-dimethylethyl)-2-methylbenzene	5.84
00488-23-3	1,2,3,4-tetramethylbenzene	<u>9.07</u>
00538-68-1	n-pentylbenzene	<u>1.70</u>
00098-19-1	1-(1,1-dimethylethyl)-3,5-DMbenzene	<u>7.50</u>
00091-20-3	naphthalene	<u>1.18</u>
00112-40-3	n-dodecane	<u>0.38</u>

CAS #	COMPOUND	MIR
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Carbonyl Compounds

<u>00050-00-0</u>	<u>formaldehyde</u>	<u>7.15</u>
<u>00075-07-0</u>	<u>acetaldehyde</u>	<u>5.52</u>
<u>00107-02-8</u>	<u>acrolein</u>	<u>6.77</u>
<u>00067-64-1</u>	<u>acetone</u>	<u>0.56</u>
<u>00123-38-6</u>	<u>propionaldehyde</u>	<u>6.53</u>
<u>00123-72-8</u>	<u>butyraldehyde</u>	<u>5.26</u>
<u>00066-25-1</u>	<u>hexanaldehyde</u>	<u>3.79</u>
<u>00100-52-7</u>	<u>benzaldehyde</u>	<u>-0.55</u>
<u>00078-93-3</u>	<u>methyl ethyl ketone (2-butanone)</u>	<u>1.18</u>
<u>00078-85-3</u>	<u>methacrolein</u>	<u>6.77</u>
<u>04170-30-3</u>	<u>crotonaldehyde</u>	<u>5.42</u>
<u>00110-62-3</u>	<u>valeraldehyde</u>	<u>4.41</u>
<u>00620-23-5</u>	<u>m-tolualdehyde</u>	<u>-0.55</u>

**List of ~~Light End~~ and Mid-Range Hydrocarbons Compounds
(Listed by CAS number)**

<u>00050-00-0</u>	<u>formaldehyde</u>
<u>00620-23-5</u>	<u>m-tolualdehyde</u>
<u>00064-17-5</u>	<u>ethanol</u>
<u>00066-25-1</u>	<u>hexanal</u>
<u>00067-56-1</u>	<u>methanol</u>
<u>00067-64-1</u>	<u>acetone</u>
00071-43-2	benzene
00074-84-0	ethane <u>ethane</u>
00074-85-1	ethene
00074-86-2	ethyne
00074-98-6	propane
00074-99-7	1-propyne
<u>00075-07-0</u>	<u>acetaldehyde</u>
00075-28-5	2-methylpropane
00075-83-2	2,2-dimethylbutane
00078-78-4	2-methylbutane
00078-79-5	2-methyl-1,3-butadiene
<u>00078-85-3</u>	<u>methacrolein</u>
<u>00078-93-3</u>	<u>methyl ethyl ketone (2-butanone)</u>
00079-29-8	2,3-dimethylbutane
00091-20-3	naphthalene
00095-47-6	o-xylene
00095-63-6	1,2,4-trimethylbenzene
00095-93-2	1,2,4,5-tetramethylbenzene
00096-14-0	3-methylpentane
00096-37-7	methylcyclopentane
00098-19-1	1-(1,1-dimethylethyl)-3,5-dimethylbenzene
00098-82-8	(1-methylethyl)benzene
00099-87-6	1-methyl-4-(1-methylethyl)benzene
00100-41-4	ethylbenzene
00100-42-5	styrene
00103-65-1	n-propylbenzene
00104-87-0	p-tolualdehyde
00105-05-5	1,4-diethylbenzene
00106-97-8	n-butane
00106-98-9	1-butene
00106-99-0	1,3-butadiene
00107-00-6	1-butyne
<u>00107-02-8</u>	<u>acrolein</u>
00107-39-1	2,4,4-trimethyl-1-pentene
00107-40-4	2,4,4-trimethyl-2-pentene

00107-83-5	2-methylpentane
00108-08-7	2,4-dimethylpentane
00108-38-3	m&p-xylene
00108-67-8	1,3,5-trimethylbenzene
00108-87-2	methylcyclohexane
00108-88-3	toluene
<u>00110-62-3</u>	<u>valeraldehyde</u>
00109-66-0	n-pentane
00109-67-1	1-pentene
00110-54-3	n-hexane
00110-82-7	cyclohexane
00110-83-8	cyclohexene
00111-65-9	n-octane
00111-66-0	1-octene
00111-84-2	n-nonane
00112-40-3	n-dodecane
00115-07-1	propene
00115-11-7	2-methylpropene
<u>00123-33-6</u>	<u>propionaldehyde</u>
<u>00123-72-8</u>	<u>butyraldehyde</u>
00124-11-8	1-nonene
00124-18-5	n-decane
00135-01-3	1,2-diethylbenzene
00135-98-8	(1-methylpropyl)benzene
00141-93-5	1,3-diethylbenzene
00142-29-0	cyclopentene
00142-82-5	n-heptane
00287-92-3	cyclopentane
00463-49-0	1,2-propadiene
00463-82-1	2,2-dimethylpropane
00464-06-2	2,2,3-trimethylbutane
00488-23-3	1,2,3,4-tetramethylbenzene
00496-11-7	2,3-dihydroindene (indan)
00503-17-3	2-butyne
00513-35-9	2-methyl-2-butene
<u>00526-73-8</u>	<u>1,2,3-trimethylbenzene</u>
00527-53-7	1,2,3,5-tetramethylbenzene
00527-84-4	1-methyl-2-(1-methylethyl)benzene
00535-77-3	1-methyl-3-(1-methylethyl)benzene
00538-68-1	n-pentylbenzene
00538-93-2	(2-methylpropyl)benzene
00540-84-1	2,2,4-trimethylpentane
00542-92-7	<u>1,3-cyclopentadiene</u>
00558-37-2	3,3-dimethyl-1-butene
00560-21-4	2,3,3-trimethylpentane
00562-49-2	3,3-dimethylpentane

00563-16-6	3,3-dimethylhexane
00563-45-1	3-methyl-1-butene
00563-46-2	2-methyl-1-butene
<u>00563-78-0</u>	<u>2,3-dimethyl-1-butene</u>
00565-59-3	2,3-dimethylpentane
00565-75-3	2,3,4-trimethylpentane
00576-73-8	1,2,3-trimethylbenzene
<u>00583-48-2</u>	<u>3,4-dimethylhexane</u>
00584-94-1	2,3-dimethylhexane
00589-34-4	3-methylhexane
00589-43-5	2,4-dimethylhexane
00589-53-7	4-methylheptane
00589-81-1	3-methylheptane
00590-18-1	cis-2-butene
00590-35-2	2,2-dimethylhexane pentane
00590-73-8	2,2-dimethylhexane
00591-76-4	2-methylhexane
00592-13-2	2,5-dimethylhexane
00592-27-8	2-methylheptane
00592-41-6	1-hexene
00592-76-7	1-heptene
00611-14-3	1-methyl-2-ethylbenzene
00616-12-6	3-methyl-trans-2-pentene
00617-78-7	3-ethylpentane
00620-14-4	1-methyl-3-ethylbenzene
00622-96-8	1-methyl-4-ethylbenzene
00624-64-6	trans-2-butene
00625-27-4	2-methyl-2-pentene
00627-20-3	cis-2-pentene
00637-92-3	1-ethyl-tert-butyl-ether
00638-04-0	cis-1,3-dimethylcyclohexane
00646-04-8	trans-2-pentene
00674-76-0	4-methyl-trans-2-pentene
00691-37-2	4-methyl-1-pentene
00691-38-3	4-methyl-cis-2-pentene
00693-89-0	1-methylcyclopentene
00760-20-3	3-methyl-1-pentene
00763-29-1	2-methyl-1-pentene
00816-79-5	3-ethyl-cis-2-pentene
00822-50-4	trans-1,2-dimethylcyclopentane
00874-41-9	1,3-dimethyl-4-ethylbenzene
00926-82-9	3,5-dimethylheptane
00933-98-2	1,2-dimethyl-3-ethylbenzene
00934-80-5	1,2-dimethyl-4-ethylbenzene
00992-62-3	3-methyl-cis-2-pentene
01069-53-0	2,3,5-trimethylhexane

<u>01072-05-5</u>	<u>2,6-dimethylheptane</u>
01074-17-5	1-methyl-2-n-propylbenzene
01074-43-7	1-methyl-3-n-propylbenzene
01074-55-1	1-methyl-4-n-propylbenzene
01120-21-4	n-undecane
01120-62-3	3-methylcyclopentene
<u>01595-11-5</u>	<u>1-methyl-2-n-butylbenzene</u>
01634-04-4	1-methyl-tert-butyl-ether
<u>01640-89-7</u>	<u>ethylcyclopentane</u>
01678-91-7	ethylcyclohexane
1001 1758-88-9	1,4-dimethyl-2-ethylbenzene
02051-30-1	2,6-dimethyloctane
02091-95-6	2,2,5-trimethylheptane
02207-01-4	cis-1,2-dimethylcyclohexane
02207-03-6	trans-1,3-dimethylcyclohexane
02207-04-7	trans-1,4-dimethylcyclohexane
02213-23-2	2,4-dimethylheptane
02216-33-3	3-methyloctane
02532-58-3	cis cis-1,3-dimethylcyclopentane
02738-19-4	2-methyl-2-hexene
02870-04-4	1,3-dimethyl-2-ethylbenzene
03074-71-3	2,3-dimethylheptane
03221-61-2	2-methyloctane
03404-61-3	3-methyl-1-hexene
03522-94-9	2,2,5-trimethylhexane
03899-36-3	3-methyl-trans-3-hexene
03968-85-2	(2-methylbutyl)benzene
04032-94-4	2,4-dimethyloctane
04050-45-7	trans-2-hexene
<u>04170-30-3</u>	<u>crotonaldehyde</u>
06443-92-1	cis-2-heptene
07385-78-6	3,4-dimethyl-1-pentene
07642-04-8	cis-2-octene
07642-09-3	cis-3-hexene
07688-21-3	cis-2-hexene
10574-37-5	2,3-dimethyl-2-pentene
13269-52-8	trans-3-hexene
13389-42-9	trans-2-octene
14686-13-6	trans-2-heptene
14686-14-7	trans-3-heptene
14850-23-8	trans-4-octene
15869-87-1	2,2-dimethyloctane
15890-40-1	1-cis,2-trans; <u>(1a,2a,3b)-1,2,3-trimethylcyclopentane</u>

APPENDIX 2

DEFINITIONS AND COMMONLY USED ABBREVIATIONS

I. The abbreviations and definitions set forth in this section apply to Parts A through G of these test procedures:

<u>ASTM</u>	≡	<u>American Society for Testing and Materials</u>
Carbon No.	=	number of carbon atoms in the hydrocarbon or organic compound being measured.
CH_3OH_d	=	the methanol concentration in the dilution air as determined from the dilution air methanol sample using the procedure specified in Method No. 1001, ppmC.
CH_3OH_e	=	the methanol concentration in the dilute exhaust as determined from the dilute exhaust methanol sample using the procedure specified in Method No. 1001, ppmC.
CH_{4d}	=	the methane concentration in the dilution air, ppmC.
CH_{4e}	=	the methane concentration in the dilute exhaust, ppmC.
$\text{C}_2\text{H}_5\text{OH}_d$	=	the ethanol concentration in the dilution air as determined from the dilution air ethanol sample using the procedure specified in Method No. 1001, ppmC.
$\text{C}_2\text{H}_5\text{OH}_e$	=	the ethanol concentration in the dilute exhaust as determined from the dilute exhaust ethanol sample using the procedure specified in Method No. 1001, ppmC.
<u>CNG</u>	≡	<u>compressed natural gas</u>
CO_e	=	the carbon monoxide concentration in the dilute exhaust corrected for carbon dioxide and water removal, ppm.
CO_{em}	=	the carbon monoxide concentration in the dilute exhaust uncorrected for carbon dioxide and water removal, ppm.
CO_{2e}	=	the carbon dioxide concentration in the dilute exhaust, %.
<u>CVS</u>	≡	<u>constant volume sampler</u>

$D_{\text{phase } n}$	=	the distance driven by the test vehicle on a chassis dynamometer during test phase n (where n is either 1, 2, or 3), mile.
Dens_{ROH}	=	density of alcohol, g/mL.
DF	=	dilution factor (see Dilution Factor Calculation).
<u>FID</u>	\equiv	<u>flame ionization detector</u>
FID THC_d	=	the total hydrocarbon concentration including methane and methanol (for methanol-fueled engines) or ethanol (for ethanol-fueled engines) in the dilution air as measured by the FID, ppmC.
FID THC_e	=	the total hydrocarbon concentration including methane and methanol (for methanol-fueled engines) or ethanol (for ethanol-fueled engines) in the dilution exhaust as measured by the FID, ppmC.
<u>FTP</u>	\equiv	<u>Federal Test Procedure</u>
<u>GC</u>	\equiv	<u>gas chromatograph</u>
<u>GC/MS</u>	\equiv	<u>gas chromatography/mass spectrometry</u>
HC_{conc}	=	net concentration of an HC compound in the dilute exhaust corrected for background per test phase, ppbC.
HC_d	=	composite concentration of an HC compound in the dilution air (background) for all three test phases as determined from the composite dilution air sample using the procedure specified in Method No. 1002 and Method No. 1003, ppbC.
HC_{dens}	=	mass per unit volume of an HC compound corrected to standard conditions (293.16° K and 760 mm Hg) g/ft ³ .
HC_e	=	concentration of an HC compound in the dilute exhaust per test phase as determined from the dilute exhaust sample using the procedure specific in Method No. 1002 and Method No. 1003, ppbC.
$\text{HC}_{\text{mass } n}$	=	mass emissions of an HC compound per test phase n (where n is either 1, 2, or 3), mg.
HC_{wm}	=	total weighted mass of an HC compound per mile, g/mile.

HCHO_e	=	formaldehyde concentration in the dilute exhaust as determined from the dilute exhaust carbonyl sample using the procedure specified in Method No 1004, ppm.
HCR	=	the hydrogen-to-carbon ratio for the fuel used.
<u>HPLC</u>	=	<u>high performance liquid chromatography</u>
Iconc_{d1}	=	dilution air (background) alcohol concentration in the primary impinger for all three test phases as determined by the procedure specified in Method No. 1001, ppmC.
Iconc_{d2}	=	dilution air (background) alcohol concentration in the secondary impinger for all three test phases as determined by the procedure specified in Method No. 1001, ppmC.
Iconc_{e1}	=	dilute exhaust alcohol concentration in the primary impinger per test phase as determined by the procedure specified in Method No. 1001, ppmC.
Iconc_{e2}	=	dilute exhaust alcohol concentration in the secondary impinger per test phase as determined by the procedure specified in Method No. 1001, ppmC.
Imass_d	=	total mass of an alcohol or carbonyl compound collected from the dilution air (background) in both primary and secondary impingers for all three test phases as determined by the procedure specified in Method No. 1001 (alcohol) or Method No. 1004 (carbonyl), μg .
Imass_e	=	total mass of an alcohol or carbonyl compound collected from the dilute exhaust in both primary and secondary impingers per test phase as determined by the procedure specified in Method No. 1001 (alcohol) or Method No. 1004 (carbonyl), μg .
Itemp_d	=	dilution air temperature at the flowmeter inlet for impinger sampling, $^{\circ}\text{K}$.
Itemp_e	=	dilute exhaust temperature at the flowmeter inlet for impinger sampling, $^{\circ}\text{K}$.
Ivol_d	=	total volume of dilution air (background) bubbled through the impingers for all three test phases corrected to standard conditions (293.16°K and 760 mm Hg), liter.
Ivol_{dm}	=	total volume of dilution air (background) bubbled through the impingers for all three test phases as measured during testing, liter.

$Ivol_e$	=	total volume of dilute exhaust bubbled through the impingers per test phase corrected to standard conditions (293.16° K and 760 mm Hg), liter.
$Ivol_{em}$	=	total volume of dilute exhaust bubbled through the impingers per test phase as measured during testing, liter.
$Ivol_r$	=	volume of the reagent used in an impinger, mL.
<u>LOD</u>	≡	<u>limit of detection</u>
<u>LPG</u>	≡	<u>liquified petroleum gas</u>
Mol. Vol.	=	molecular volume which is 24.055 liter/mole at standard conditions (293.16° K and 760 mm Hg).
Mol. Wt.	=	molecular weight of the compound being measured, g/mole.
<u>NIST</u>	≡	<u>National Institute of Standards and Technology</u>
<u>NMHC</u>	≡	<u>non-methane hydrocarbons</u>
$NMHC_{conc}$	=	the non-methane hydrocarbon concentration in the dilute exhaust corrected for background, ppmC.
$NMHC_d$	=	the non-methane hydrocarbon concentration in the dilution air corrected for methane and alcohol removal, ppmC.
$NMHC_{dens}$	=	the mass per unit volume of non-methane hydrocarbon corrected to standard conditions (16.33 g/ft ³ at 293.16° K and 760 mm Hg assuming a C:H ratio of 1:1.85 for gasoline; <u>16.78 g/ft³ at 293.16° K and 760 mm HG assuming a C:H ratio of 1:1.94 for Phase 2 reformulated gasoline</u> ; <u>19.52 g/ft³ at 293.16° K and 760 mm HG assuming a C:H ratio of 1:3.78 for natural gas</u> ; and <u>17.28 17.26 g/ft³ for LPG at 293.16 K and 760 mm Hg assuming a C:H ratio of 1:2.64</u>), g/ft ³ .
$NMHC_e$	=	non-methane hydrocarbon concentration in the dilute exhaust corrected for methane and alcohol removal, ppmC.
$NMHC_{mass\ n}$	=	the mass emission of non-methane hydrocarbon per test phase n (where n is either 1, 2, or 3), g.
$NMHC_{wm}$	=	the total weighted mass of non-methane hydrocarbon per mile for all three phases of the FTP, g/mile.

<u>NMOG</u>	≡	<u>non-methane organic gases</u>
P_B	≡	<u>barometric pressure during testing, mm Hg.</u>
<u>PID</u>	≡	<u>photoionization detector</u>
<u>PLOT</u>	≡	<u>porous layer open tubular</u>
R_a	=	the relative humidity of the ambient air, %.
r_{CH_3OH}	=	the FID response factor to methanol (see CFR 40, 86.121-90(c)).
r_{CH_4}	=	the FID response factor to methane (see Part B, "Determination of NMHC by FID").
$r_{C_2H_5OH}$	=	the FID response factor to ethanol (same procedure for methanol response factor, see CFR 40, 86.121-90(c)).
RHO	=	generic symbol representing a carbonyl compound such as formaldehyde, acetaldehyde, acetone, etc.
RHO_{conc}	=	net concentration of a carbonyl compound in the dilute exhaust corrected for background per test phase, ppm.
RHO_d	=	composite concentration of a carbonyl compound in the dilution air (background) for all three test phases, ppm.
RHO_{dens}	=	mass per unit volume of a carbonyl compound corrected to standard conditions (293.16°K and 760 mm Hg), g/ft ³ .
RHO_e	=	concentration of a carbonyl compound in the dilute exhaust per test phase, ppm.
$RHO_{mass\ n}$	=	mass emissions of a carbonyl compound per test phase n (where n is either 1, 2, or 3), g.
RHO_{wm}	=	total weighted mass emissions of a carbonyl compound per mile, g/mile.
ROH	=	generic symbol representing an alcohol compound such as methanol or ethanol.
ROH_{conc}	=	net concentration of an alcohol compound in the dilute exhaust corrected for background per test phase, ppm.

ROH_d	=	composite concentration of an alcohol compound in the dilution air (background) for all three test phases, ppm.
ROH_{dens}	=	mass per unit volume of an alcohol compound corrected to standard conditions (293.16° K and 760 mm Hg), g/ft ³ .
ROH_e	=	concentration of an alcohol compound in the dilute exhaust per test phase, ppmC.
$ROH_{mass\ n}$	=	mass emissions of an alcohol compound per test phase n (where n is either 1, 2, or 3), g.
ROH_{wm}	=	total weighted mass emissions of an alcohol compound per mile, g/mile.
<u>SAE</u>	≡	<u>Society of Automotive Engineers</u>
<u>SRM</u>	≡	<u>Standard Reference Material</u>
VMIX	=	the total dilute exhaust volume measured per test phase and corrected to standard conditions (293.16° K and 760 mm Hg), ft ³ .

II. The following list is commonly used measurement abbreviations:

<u>m</u>	≡	<u>meter</u>
<u>cm</u>	≡	<u>centimeter</u>
<u>μm</u>	≡	<u>micrometer</u>
<u>μ</u>	≡	<u>micron</u>
<u>L</u>	≡	<u>liter</u>
<u>mL</u>	≡	<u>milliliter</u>
<u>μL</u>	≡	<u>microliter</u>
<u>ppb</u>	≡	<u>parts per billion.</u>
<u>ppbC</u>	≡	<u>parts per billion carbon equivalent.</u>
<u>ppm</u>	≡	<u>parts per million.</u>
<u>ppmC</u>	≡	<u>parts per million carbon equivalent.</u>

APPENDIX 3

REFERENCES

- [1] Code of Federal Regulations, Title 40, Part 86, Subpart B
- [2] SAE J254, "Instrumentation and Techniques for Exhaust Gas Emissions Measurement"
- [3] SAE J1094a, "Constant Volume Sampler System for Exhaust Emissions Measurement"
- [4] SAE 770141, "Optimization of a Flame Ionization Detector for Determination of Hydrocarbons in Diluted Automotive Exhausts". G.D. Reschke, Vehicle Emissions Laboratory, General Motors Proving Ground
- [5] SAE J1154, "Methane Measurement Using Gas Chromatography," (revised December 1991)
- [6] U.S. Environmental Protection Agency, Characterization of Exhaust Emissions from Methanol and Gasoline Fueled Automobiles, EPA 460/3-82-004.
- [7] U.S. Environmental Protection Agency, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, (Method T03-15) EPA-600/4-89-017 Research Triangle Park, North Carolina, June, 1989.
- [8] Standard Test Method for C₁ through C₆ Hydrocarbons in the Atmosphere by Gas Chromatography, American Standards for Testing Materials (ASTM) Standards on Chromatography (1981).
- [9] U.S. Environmental Protection Agency, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, (Method T03-15) EPA-600/4-84-041 Research Triangle Park, North Carolina, April, 1989.
- [10] Hull, L.A., Procedures for 2,4-Dinitrophenylhydrazone Aldehyde-Ketone Air Analysis, Internal Report at U.S. EPA.
- [11] Shriner, R.L. and Fuson, R.C., Identification of Organic Compounds, 2nd. Ed., John Wiley and Sons, Inc., 1940, p. 143.